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THE FLUORINATION OF URANIUM FROM DRIED SOLIDS AND ITS
APPLICATION TO THE FLUORIDE VOLATILITY PROCESS

by

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THE FLUORINATION OF URANIUM FROM DRIED SOLIDS AND ITS APPLICATION TO THE FLUORIDE VOLATILITY PROCESS

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ABSTRACT

The ADF fluoride volatility process employs the unit processes of dissolution, fluidized bed drying and fluorination to recover fissile material from reactor fuels. Variables that affect the removal from dried solids representative of those obtained from dissolver solutions of high zirconium alloy fuels were studied. Variables investigated were particle size, additives, temperature, time, hydrofluorination and pyrolysis. Application of the study to Dresden and APPR type fuels was also considered.

I. INTRODUCTION

Until recently, fluoride volatility processes have involved the fluorination of uranium in a liquid phase, either in a fused salt or an interhalogen liquid. These processes have the disadvantages that plutonium cannot be converted to plutonium hexafluoride in the interhalogen media, corrosion is severe in fused salt media, and hazards exist in the case of interhalogen liquids. For these reasons fluorination of uranium and plutonium in the solid phase at elevated temperatures has been considered. Because the heat evolved in the fluorination reaction can be very high, the use of fluidized beds is advantageous in controlling the gas-solid reaction.

Before fissile material can be fluorinated it is necessary to convert the fuel into a form which can be reacted with fluorine. Most alloying or cladding materials, such as zirconium, stainless steel and aluminum, are not attacked by fluorine at reasonable temperatures. One approach consists of dissolving the fuel in aqueous media and following it with a fluidized-bed drying step before fluorination. This approach should be applicable to virtually all reactor fuels.

The term, ADF volatility process, has been applied to the general fuel recovery scheme which involves aqueous dissolution of the fuel, drying of the solution to solids, and subsequent fluorination of the solids to recover fissile material, as uranium and plutonium hexafluorides, after which the solids can be discarded as waste. When, for example, it is applied to

zirconium alloy fuels, the process involves dissolution of the alloy in hydrofluoric acid containing an oxidant, followed by conversion of the solution to dry granular solids by spraying the solution into a heated fluidized bed of granular material. The solids may then be fluorinated in fluidized or static beds to remove the uranium as the volatile uranium hexafluoride. The process can be utilized for other fuels and varies only in the mode of dissolution of the fuel.

In order to establish the feasibility of the process it has been necessary to demonstrate that the drying step and the fluorination step were satisfactory. The fluidized bed drying of solutions containing zirconium, in concentrations simulating that which would be obtained from enriched zirconium alloy fuels, has been adequately demonstrated in Argonne Chemical Engineering pilot plant operations (ANL-5996, p. 139; ANL-6029, p. 85; ANL-6068, p. 93). It has also been necessary to demonstrate that uranium can be quantitatively removed from the dried solids by reaction with fluorine at elevated temperatures. The practicability of the process depends upon the conditions necessary for the recovery of uranium from the dried solids. Laboratory work has been completed to demonstrate the conditions necessary for removal of uranium by fluorination from dried solids of zirconium alloy fuels, uranium oxide fuels of the Dresden type and stainless steel fuels of the APPR type. This report covers the research program dealing with the investigation of the variables of the fluorination step in the process.

The variables which came under consideration were: the effect of particle size in gas-solid reactions; the addition of metals as an aid to fluorination; the temperature of fluorination; the time needed for complete uranium removal; the effect of hydrofluorination pretreatment of the dried solids before fluorination; the possible sublimation of zirconium tetrafluoride; and the effect of pyrolysis of the fluorinated residue prior to refluorination.

II. EXPERIMENTAL

A. Materials

Materials used simulated those that would be obtained from the dissolution and calcination of zirconium alloy fuels, Dresden⁽¹⁾ fuels and APPR⁽²⁾ fuels. Solids were prepared from solutions representative of those obtained from the dissolved fuels. For the zirconium alloy fuel the solution contained 0.02 M $\text{UO}_2\text{F}_2 \cdot 1.5 \text{ M } \text{ZrF}_4$ with a F/Zr ratio of 4.5/1. The Dresden type solution was prepared having the following composition: 0.44 M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.13 M $\text{ZrF}_2(\text{NO}_3)_2$, and 3.55 M HNO_3 . A synthetic APPR feed solution was prepared using the data of Cunningham and Beaver.⁽²⁾ The solution composition, with the deletion of the boron carbide, was 0.51 M $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$, 1.75 M $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{ H}_2\text{O}$, 0.08 M $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$, 2 M HCl and 6 M HNO_3 .

Two general types of samples were used in the fluorination experiments. One was obtained by drying the aqueous feed solutions at 300 - 350 C in a laboratory calciner. This was done by adding the feed solution dropwise to a heated tube, which has an internal stainless steel drying cup which served as a collecting surface, while the system was partially evacuated. The drying temperature was obtained from a thermocouple placed inside the drying column. The resulting solids were ground before fluorination. The other type of sample was obtained from the Argonne Chemical Engineering pilot-plant group. It was made by spray drying the solution, representative of high zirconium fuels in fluid-beds. Because of the varied complexity of these pilot plant materials, their make-up and history are summarized in Table I.

High purity fluorine was obtained from the General Chemical Company and prior to use the fluorine was passed through a heated bed of sodium fluoride to remove traces of hydrogen fluoride. Helium was used after passing it through Linde Molecular Sieves to remove moisture.

B. Apparatus

Fluorination experiments were performed in an apparatus in which fluorine was passed over a sample in a nickel boat within a tube furnace. The apparatus was constructed from nickel components and $\frac{1}{4}$ -inch OD nickel tubing which were either silver-soldered together or joined by Teflon gasketed, flared connectors. Hoke 413 diaphragm valves were used throughout the system.

The tube furnace was made from a 14-inch length of 1-inch OD, schedule 40 nickel pipe. The front end was fitted with a Teflon gasketed, water cooled flanged cover and gas entry tube. The rear of the furnace was fitted with a $\frac{1}{4}$ -inch nickel tube for gas exit and a $\frac{1}{4}$ -inch OD nickel thermocouple well which extended into the furnace about $3\frac{1}{2}$ inches, thus positioning the sample boat in the center of the furnace. The tube furnace was fitted with a hemi-cylindrical slide to allow flat-bottomed boats to be used. The sample boats, 0.8 x 4.0 x 0.2 inches, were made from 16 mil nickel sheet and were welded at the corners. The various components of the apparatus were joined to a manifold which was provided with cold-traps and sources of vacuum, helium and fluorine.

The exit line from the furnace tube led to a pair of traps, connected in series and cooled with a dry-ice trichloroethylene mixture used for collection of uranium hexafluoride. The traps were standard $\frac{3}{4}$ -inch flare traps fitted with $\frac{1}{2}$ -inch diameter nickel test tubes. A fluorine disposal system, consisting of a cylindrical brass vessel filled with activated alumina, to react with the excess fluorine, was used in the exit stream.

Table I

SUMMARY OF PILOT PLANT MATERIALS

Run Number	ZCP-38	ZCP-47	ZCP-50	ZCP-59	ZCP-60	ZCP-66	ZCP-69	ZCP-71
Bed Temp, (C)	300	300	300	300	300	240	240	350
Starting Bed	CaF ₂	CaF ₂	ZrO ₂ precoated with ZrF ₄	ZrO ₂	ZCP-59	ZCP-60	ZCP-66	ZCP-69
Feed Composition	1.5 M Zr 6.8 M F 0.022 M U	1.4 M Zr 6.1 M F 0.013 M U	1.3 M Zr 6.4 M F 0.026 M U	1.3 M Zr 5.8 M F 0.0058 M U	1.2 M Zr 7.0 M F 0.0097 M U	1.2 M Zr 5.8 M F 0.011 M U	1.4 M Zr 16 M F 0.0011 M U	1.3 M Zr 14 M F 0.0005 M U
Feed Preparation	Dissolve UO ₂ F ₂ and ZrF ₄ in aq. HF at 75 C. Add SnCl ₂ to reduce U ⁺⁶ .	Dissolve UO ₂ F ₂ and ZrF ₄ in aq. HF at 75 C. 1% SnF ₄ added.	Feed soln from Gen- eral Chem- ical Co.	Dissolve UO ₂ F ₂ and ZrF ₄ in aq. HF at 75 C. 1.5% Sn and small amts. NiCrFe added.	Feed soln from Gen- eral Chem- ical Co.	Dissolved 300 C dryer products in proper amt. of aq. HF.	Material pre- viously calcined at 240 C, dis- solved in HF.	Material pre- viously calcined at 300 C, dissolved in hydrofluoric acid.
Analysis of Solids, w/o ^a	47.0 Zr 41.8 F ₂ 1.69 U 3.5 O ₂	11.9 Zr 4.02 F ₂ 0.62 U --	51.0 Zr 32.6 F ₂ 2.53 U --	-- -- 0.76 U --	54.8 Zr 30.9 F ₂ 1.02 U 6.5 O ₂	47.0 Zr 40.6 F ₂ 00.77 U 4.0 O ₂	48.0 Zr 42.4 F ₂ 0.55 U --	48.0 Zr 32.4 F ₂ 0.55 U
Total Run Time, (hrs)	70	11	40	60	12	51	41.5	54.5
Remarks	During calcina- tion an HF side stream boosted the F/Zr mole ratio to 10	Bed material only thinly coated with uranium			Jet attri- tion used to reduce particle size (total run 72 hrs)	Solids separated from feed at room temp. Feed temp. 55 C.		Starting bed was heated slowly from 240-350 C to mini- mize agglomeration

^aResidual amts are calcium, water

C. Procedure

The experimental procedure used was as follows. About 15 grams of material to be fluorinated were weighed into a tared nickel boat, which was positioned against the thermocouple well in the tube furnace. Helium was passed over the sample while the furnace was brought to the reaction temperature. When temperature equilibrium had been reached fluorine was substituted for helium and the flow was adjusted to the desired rate using a calibrated thermal flow meter. Any uranium hexafluoride that was formed was condensed and collected in the cold traps. At the completion of the fluorination helium was substituted for the fluorine and the sample allowed to cool in a helium atmosphere. Uranium analyses were obtained by X-ray fluorescence measurements on the initial material and on the final residue taken from the boat. All materials were ground to minus 200 mesh for this analysis.

III. RESULTS AND DISCUSSION

Before embarking on a discussion of the results it is appropriate to re-iterate the general purpose of the experiments. In all of these experiments the purpose was to see the effect of the variables on the removal of uranium from the dried solids by fluorination. The fluidized bed dried solids of the zirconium alloy fuels were used for the major portion of this investigation. Very little loss of uranium can be tolerated in the discarded waste in the ADF process for the zirconium matrix fuel and similarly enriched fuels. Therefore, because of the low concentrations involved, and the difficultly soluble zirconium fluoride matrix, it was necessary to use the analytical technique of X-ray fluorescence (see Appendix I). The lowest detectable concentration of uranium was 0.008 w/o. A removal of uranium from the dried solid to this concentration would insure a recovery of better than 99 per cent of the uranium in the original fuel. It was thus the goal of these experiments to establish the conditions of the fluorination step in the ADF process which would yield a final fluorinated material low enough in uranium content so that it could be discarded as waste.

A. Effect of Particle Size

Results from experiments on the effect of particle size on uranium removal are given in Table II. The materials prepared in the laboratory (L-materials) show essentially the same uranium removal regardless of size. Best overall removal in these experiments was obtained with ZCP-47, a calcium fluoride matrix material. Preliminary experiments had suggested that higher uranium removal was obtained from small particles. Pursuing this further, various pilot-plant drier products were ground in a ball mill for 24 hours and then fluorinated. Results from experiments on fluorination

of ball milled materials are given in Table III. Ball milling appears to be ineffective on material ZCP-38, somewhat effective on ZCP-59, ZCP-69, and ZCP-71, and very effective on ZCP-66. Due to a wide variation in the composition of the drier products, it is difficult to say exactly why the solids differ so markedly on fluorination, but it does appear that particle size is not the controlling factor for uranium removal.

Table II

EFFECT OF PARTICLE SIZE ON URANIUM REMOVAL

	Reactor Temperature		600 C	
	Time for Experiment		2 hrs	
	Fluorine Flow Rate		11 g/hr	
	Uranium Concentration (w/o)			
Material ^a	Initial	Final	Particle Size (microns)	Uranium Removed (%)
ZCP-47	0.53	0.015	250 - 420	97
ZCP-47	0.76	0.016	105 - 149	98
ZCP-47	0.84	0.037	62 - 105	95.7
L-1	1.10	0.12	All sizes	89.1
L-1	1.13	0.12	250 - 420	89.4
L-1	1.30	0.11	105 - 149	90.9
L-2	1.16	0.075	177 - 250	93.5

^aAll materials with code ZCP were produced by the Argonne Chemical Engineering Pilot Plant Group and are described in Table I. All materials with code L, were produced in the laboratory following the procedure outlined in the experimental section.

Table III

EFFECT OF BALL MILLING ON URANIUM REMOVAL

		Time for Experiment	2 hrs
		Fluorine Flow Rate	12 g/hr
		% Uranium Remaining after Fluorination	
Material ^a	Temperature (C)	Original (~100-160 mesh)	Ball-Milled (~325 mesh)
ZCP-38	450	84.0	77.3
	600	16.0	15.7
ZCP-59	450	59.5	21.0
	600	9.1	3.8
ZCP-66	450	65.5	56.3
	600	50.7	6.3
ZCP-69	450	61.8	50.0
	600	12.2	9.5
ZCP-71	450	69.2	39.2
	600	8.2	5.3

^aSee Table I for compositions

B. Additives

In a Brookhaven National Laboratory report⁽³⁾ on the removal of protactinium from thorium fluoride, "metals were added to the thorium fluoride matrix in the hope that induced lattice defects would facilitate uranium removal by increasing its diffusion rate out of the solid." A somewhat similar technique was applied to the zirconium solids. It was hoped that the added metal fluoride would act as an internal fluorinating agent or catalyst. The metal fluorides were added to the feed solutions before drying, in concentrations approximately equal to that of the uranium in weight per cent.

Results of these experiments are shown in Table IV. Except for lead, the additives do not appear to have appreciably enhanced the removal of uranium. The use of lead resulted in corrosion of the nickel boat which was so severe that its use is impractical.

Table IV

EFFECT OF ADDITIVES ON URANIUM REMOVAL

	Reactor Temperature		600 C	
	Time for Experiment		2 hrs	
	Fluorine Flow Rate		11 g/hr	
	Uranium Concentration (w/o)			
<u>Material</u>	<u>Initial</u>	<u>Final</u>	<u>Additive</u>	<u>Uranium Removed (%)</u>
L-1	1.10	0.12	-	89.1
L-1	1.11	0.09	Co ^{++a}	92.0
L-1	1.07	0.04	Pb ^{++a}	96.3
L-2	1.16	0.075	-	93.5
L-2	1.14	0.070	Sn ^{++a}	93.8

^aWeight per cent of added metal approximately equal to the initial uranium concentration

C. Effect of Temperature

Data from experiments on the effect of temperature on uranium removal have been tabulated in Table V and plotted in Figure 1 as log per cent of uranium remaining in the solid versus the reciprocal of the absolute temperature. All data indicate that a temperature of about 650 C is needed for complete uranium removal.

Table V

EFFECT OF TEMPERATURE ON URANIUM REMOVAL

Material	Time for Experiment Fluorine Flow Rate		2 hrs 12 g/hr	
	Uranium Concentration		Temp (C)	Uranium Removed (%)
	Initial	Final		
ZCP-38	1.69	1.42	450	16.0
38	1.69	0.27	600	84.0
47	0.63	0.086	450	86.3
47	0.63	0.027	600	95.7
50	2.60	0.39	450	84.0
50	2.60	0.033	600	98.7
50	2.60	0.014	650	99.5
59	0.76	0.64	300	15.7
59	0.76	0.54	400	29.0
59	0.76	0.30	500	60.5
59	0.76	0.069	600	90.9
59	0.76	<0.008	650	>99.2
60	1.02	0.92	300	10.0
60	1.02	0.50	450	51.0
60	1.02	0.28	525	72.6
60	1.02	0.048	600	95.3
60	1.02	<0.008	650	>99.2
66	0.77	0.59	300	23.4
66	0.77	0.55	400	29.6
66	0.77	0.47	500	38.8
66	0.77	0.37	600	49.4
69	0.55	0.34	450	28.2
69	0.55	0.27	525	51.0
69	0.55	0.067	600	87.8
71	0.55	0.38	450	31.0
71	0.55	0.19	525	65.5
71	0.55	0.045	600	91.0

Figure 1

EFFECT OF TEMPERATURE ON URANIUM REMOVAL

Solid ZCP-66 was an exception to this generality, for it gave poor uranium removal at all temperatures. X-ray diffraction analysis on ZCP-66 indicates that zirconium tetrafluoride was the major species present, with zirconium tetrafluoride monohydrate as the minor phase. Analytical results, as shown in Table VI indicate that ZCP-66 contains a larger amount of water than previous drier products. Thus, when heating

Table VI

CHEMICAL ANALYSIS

Material	Zirconium (%)	Fluoride (%)	Oxygen (%)	Material Volatile at 450 C		
				HF (%)	H ₂ O (%)	F/Zr Mol Ratio
Dryer Product ZCP-60	54.8	30.9	6.5	1.5	0.4	2.71
Same, after Hydrofluorination	49	41.3	1.70	3.6	0.11	4.05
Dryer Product ZCP-66	47	40.6	4.03	3.4	1.8	4.15
Same, after Hydrofluorination	46	43.4	1.03	3.3	0.43	4.53

ZCP-66 prior to fluorination, hydrolysis probably occurs resulting in the formation of zirconium dioxide. The zirconium dioxide formed may inhibit uranium removal by actively competing for the available fluorine.

Solids ZCP-59 and ZCP-60 show excellent uranium removal, the final residue containing less than 0.008 w/o uranium. When analyzed by X-ray diffraction techniques the materials ZCP-59 and ZCP-60 were shown to have zirconyl fluoride as the major species present with zirconium tetrafluoride and zirconium tetrafluoride monohydrate being there in minor amounts.

The slight temperature effect on ZCP-47 was probably caused by having the uranium in a thin coating on the calcium fluoride bed material. For solid ZCP-59, this same phenomenon was probably due to a high percentage of zirconium dioxide in the core, which generated large quantities of heat when reacting with fluorine, causing high temperatures in individual particles and thus aiding in uranium removal. From these data it appears that the fluid bed calciner should be operated in a manner which will yield drier products free of hydrated zirconium compounds.

D. Effect of Duration of Fluorination

When experiments on the effect of temperature on uranium removal did not yield complete removal it was felt that possibly the length of time of fluorination should be increased. Therefore, experiments were run testing the effect of fluorination time on uranium removal. Data from these experiments are given in Table VII and plotted in Figure 2 as per cent uranium removed versus time of fluorination.

These data show that all materials appear to reach a point beyond which uranium removal becomes exceedingly difficult. It is not clear exactly what causes this trouble. It may be compound formation or it may be a sintering phenomenon which alters the surface of the material to such an extent that the rate of uranium removal appears constant over the latter period of the experiment.

Experiments on the effect of time on uranium removal on sample ZCP-59 were designed to maintain the ratio of sample weight to fluorine flow a constant. This was done so as not to bias the short time runs unfavorably. In all cases the final uranium content was less than 0.008 weight per cent which is the lowest concentration detectable.

E. Effect of Hydrofluorination

Experiments have been run evaluating the effect of hydrofluorination of the solid prior to fluorination. Anhydrous hydrogen fluoride was passed over the sample for two hours at 450 C, after which the samples were then fluorinated.

Table VII

EFFECT OF TIME OF FLUORINATION ON URANIUM REMOVAL

Material ^a	Uranium Concentration (w/o)		Fluorine Flow (g/hr)	Time (hrs)	Temp (C)	Uranium Removed (%)
	Initial	Final				
ZCP-59	0.76	0.71	12	1.0	300	7.2
59	0.76	0.64	12	2.0	300	15.7
59	0.76	0.66	12	3.0	300	13.1
59	0.76	0.66	12	4.0	300	13.1
ZCP-60	1.02	0.85	12	1.0	525	16.8
60	1.02	0.28	12	2.0	525	72.6
60	1.02	0.70	12	4.0	525	70.4
60	1.02	0.21	12	6.0	525	79.4
60	1.02	0.27	6	2.0	525	73.6
60	1.02	0.20	6	6.0	525	80.4
ZCP-59	0.76	<0.008	3.9	0.5	650	>99
59	0.76	<0.008	7.7	1.0	650	>99
59	0.76	<0.008	14.9	2.0	650	>99

^aSee Table I for compositions

Figure 2

EFFECT OF TIME ON URANIUM REMOVAL

Data from these experiments are given in Table VIII. The only materials whose behavior on fluorination was improved was ZCP-66. Consulting Table VI, it is noticed that the water content was appreciably reduced by treatment with anhydrous hydrogen fluoride. This, it would appear that this pretreated material would undergo little or no oxide formation on heating prior to fluorination. Solid ZCP-44 (about 30 per cent zirconium dioxide) and solid ZCP-60 (about 60 per cent zirconyl fluoride) appear to have been changed in an unsatisfactory manner by the hydrogen fluoride pretreatment.

Table VIII
EFFECT OF HYDROFLUORINATION ON
URANIUM REMOVAL

Time for Experiment		2 hrs	
Temperature of Hydrofluorination		450 C	
Temperature of Fluorination		600 C	
		Final Uranium Concentration, (w/o)	
Material	Initial Uranium Concentration (w/o)		
		No Pretreatment	After Hydrofluorination
ZCP-44	1.82	0.27	0.58
ZCP-60	1.02	0.04	0.13
ZCP-66	0.77	0.39	0.23

F. Sublimation of Zirconium Tetrafluoride

After a number of fluorinations on various materials it became apparent that a new approach should be taken. If a large quantity of zirconium tetrafluoride were to be sublimed from the sample it was hoped that this would reduce the role of the matrix material to an extent that satisfactory uranium removals could be obtained. Therefore, some effort was given to attempts at sublimation of zirconium tetrafluoride from the fluidized bed dried solids.

Choice of the proper temperature for sublimation was dictated by two factors. Zirconium tetrafluoride has a vapor pressure one mm at 650 C and 760 mm at 903 C;⁽⁴⁾ therefore, something above 700 C is needed for adequate removal. For purposes of this discussion the assumption was made that uranyl fluoride is the predominant uranium containing species present in pilot plant drier products. Sublimation of uranyl fluoride becomes important at 825 C;⁽⁵⁾ therefore, 800 C was chosen as an upper limit for sublimation.

A sample of ZCP-69 was subjected to sublimation under helium flow and a second sample to sublimation under reduced pressure of about 0.1 mm. The first sublimation was done at 800 C for an eight-hour period and the second sublimation at 750 C for a six-hour period. In both experiments the residue remaining after sublimation was severely caked and quite difficult to remove from the nickel boat for grinding prior to fluorination.

The data of Table IX indicate no improvement in uranium removal over what had been found before. In addition, the problems encountered in removing the sublimed residue from the sublimation vessel makes this a very unattractive route.

Table IX

URANIUM REMOVAL FROM SUBLIMED MATERIAL

Time for Experiment				2 hrs	
Fluorine Flow Rate				12 g/hr	
Temperature of Fluorination				600 C	
Total Pressure	Temp of Sub. (C)	Time of Sub. (hr)	Weight Loss (%)	Uranium Concentration	
				After Sublimation	After Fluorination
He 1 atmos.	800	8	35.0	0.63	0.071
Reduced Press. ~0.1 mm	750	6	73.5	1.15	0.038

G. Effect of Pyrolysis

In a large number of experiments the major fraction of the uranium was removed rapidly at temperatures as low as 500 C, but higher temperatures were required to remove the last 5 - 10 per cent. This suggests that some small fraction of the uranium is held tightly by chemical bonding in the zirconium fluoride matrix. To bring about a change in the structure and supposedly the forces holding the uranium, the fluorinated material was subjected to an aqueous hydrogen fluoride pyrolysis. The material used for these experiments was ZCP-50. Initially, ZCP-50 had been fluorinated for a four-hour period, leaving a final uranium concentration in the fluorinated residue to about 0.14 w/o. This "fluorinated residue" was then reacted with 1 M aqueous hydrogen fluoride in a fluidized bed at 300 C for 13.3 hours. The F/Zr weight ratio was initially 3.88. After reaction with aqueous

hydrogen fluoride, the F/Zr weight ratio dropped to 2.41. The "fluorinated residue" and the pyrohydrolyzed residue were then fluorinated for two hours at the temperatures indicated in Table X.

Table X
EFFECT OF PYROHYDROLYSIS ON
URANIUM REMOVAL

Time for Experiment Fluorine Flow Rate		2 hrs 12 g/hr	
Material	Temperature (C)	Uranium Concentration (w/o)	
		Initial	Final
Fluorinated Residue	600	0.11	0.09
Pyrohydrolyzed Residue	450	0.14	0.13
Pyrohydrolyzed Residue	525	0.14	0.034
Pyrohydrolyzed Residue	600	0.14	<0.008

As may be seen from the data of Table X, pyrohydrolysis has aided markedly in uranium removal. Unfortunately, pyrohydrolysis does not appear too attractive as a process step because of added cost in fluorine and the need for a separate vessel for this particular step.

IV. APPLICATION TO DRESDEN AND APPR TYPE FUELS

Early interest was primarily in the application of the ADF process scheme to zirconium alloy fuels. Because current developments in reactor design have resulted in a variety of fuel element materials it appeared profitable to expand this work to include fuels typical of those in present use in power reactors. The Dresden⁽¹⁾ fuel and the APPR⁽²⁾ fuel were chosen. The Dresden fuel is composed of high density uranium dioxide in Zircaloy cladding and the APPR fuel is made up of enriched uranium dioxide in a stainless steel compact.

Data from experiments on the effect of fluorination temperature on uranium removal from Dresden and APPR type fuels are given in Table XI. Application of the ADF process scheme to Dresden type fuels appears

promising. Recovery of uranium at 600 C was very good. The few data on the APPR fuel appear to indicate a general similarity to the high zirconium fuels indicating that temperatures above 650 C would probably be necessary to obtain satisfactory uranium removal upon fluorination.

Table XI

EFFECT OF TEMPERATURE ON URANIUM REMOVAL
FROM CALCINED DRESDEN AND APPR TYPE FUELS

Fluorine Flow Rate 12 g/hr					
Material	Uranium Concentration (w/o)		Fluorine Flow Time (hr)	Fluorination Temperature (C)	Uranium Removed (%)
	Initial	Final			
Dresden	73.5	58.8	1	350	20
Dresden	73.5	9.55	1	450	87
Dresden	73.5	1.47	1	550	98
Dresden	73.5	0.735	1	600	99
APPR	10.9	3.82	2	450	65
APPR	10.9	3.60	2	525	67
APPR	10.9	0.545	2	600	95
APPR	10.9	0.763	2	650	93

V. SUMMARY

The action of elemental fluorine on dried solids representative of those obtained from the fluid bed drying of dissolver solutions of high zirconium alloy fuels, Dresden and APPR fuels, was studied under a variety of conditions. The experimental results indicate that the most important factor was temperature. In general, temperatures in excess of 650 C were needed to insure complete removal of uranium from the solid. Satisfactory removal of uranium from the solids representative of the Dresden fuel was obtained at 600 C.

Pyrolysis with hydrogen fluoride of previously fluorinated materials was the only treatment that significantly aided the removal of uranium from the zirconium solid by fluorination at a temperature of 600 C.

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APPENDIX I

X-RAY SPECTROCHEMICAL DETERMINATION OF URANIUM
IN URANIUM-ZIRCONIUM FLUORIDES

The X-ray spectrochemical method of analysis as employed in the analysis of drier products and fluorination residues encountered in the ADF fluoride volatility process consists primarily of comparing the UL_{α_1} X-ray emission line intensity of an unknown with that from known uranium-zirconium fluoride mixtures. Analysis was made directly on about three grams of the powdered mixture; dissolution and chemical separation are not required.

Standards for this analysis are prepared by flash drying 10 M hydrofluoric acid solutions containing known quantities of uranium and zirconium. Subsequent reaction of the zirconium tetrafluoride monohydrate, the major zirconium species produced in the flash-drying operation, may then be employed in order to yield uranium in other zirconium matrices such as zirconium tetrafluoride or zirconyl fluoride.

A typical intensity-composition calibration plot used in the analysis of fluorinated residues is depicted in Figure 3. The standards used in the plot are flash dried preparations that have been subsequently hydrofluorinated to yield uranium in a zirconium tetrafluoride matrix.

Figure 3

PLOT OF UL_{α_1} X-RAY INTENSITY
VS WEIGHT PER CENT URANIUM
IN ZIRCONIUM TETRAFLUORIDE
MATRIX