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THE FUSED SALT-FLUORIDE VOLATILITY PROCESS FOR RECOVERING URANIUM

G. I. Cathers
M. R. Bennett
R. L. Jolley

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section A

THE FUSED SALT-FLUORIDE VOLATILITY PROCESS FOR RECOVERING URANIUM

G. I. Cathers, M. R. Bennett, R. L. Jolley

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ABSTRACT

A fluoride volatility process for recovering enriched uranium from UF_4-NaF-ZrF_4 melts, produced by the dissolution of reactor fuel elements in molten NaF-ZrF_4 through hydrofluorination, is described. The UF_4 is fluorinated to UF_6, which volatilizes, and is separated from volatile fission products in a NaF absorption-desorption cycle. In laboratory studies gross beta and gamma decontamination factors of 10^5 with a uranium loss of less than 0.1% were secured. The product UF_6 may be conveniently returned to UF_4 or metal for further use as reactor fuel.

Chemical studies, supplementary to process development work, showed that impurities, possibly oxides, have a much greater effect in the fused salt-fluorination step than such factors as use of nitrogen with the fluorine, or the method of introducing the fluorine into the fluoride melt. The colloidal behavior of NiF_2, a slightly soluble corrosion product formed in the fluorination, indicated that this material would not interfere in molten salt handling if the fused salt was not allowed to stand without agitation for prolonged periods. The absorption of UF_6 in NaF was found to be due to the formation of a UF_6-NaF complex. The equilibrium between gaseous UF_6 and solid complex was established for the temperature range of 80 to 320°C. Decomposition of the UF_6-NaF complex to a UF_5-NaF complex does not lead to appreciable uranium loss in the process if specified process conditions are maintained.

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1.0 INTRODUCTION

A new approach to processing of enriched uranium civilian power reactor fuels by a fluoride volatility method has been reported.[1,2] The method consists in three steps: dissolution of the metal or alloy in a fluoride melt by hydrofluorination, volatilization of UF_6 from the molten salt through fluorination, and final purification of the UF_6 from volatile or entrained fission product fluorides by absorption or distillation. A typical salt composition is 50-50 mole % $NaF-ZrF_4$, with a melting point of about 510°C. The second step appears feasible with use of either elemental fluorine or bromine pentafluoride. The ORNL development program on this process has been directed toward use of elemental fluorine in the second step and absorption of the UF_6 on NaF as a means of completely decontaminating the UF_6 product from fission product activity.

A practicable process flowsheet for the fused salt-fluorination and NaF decontamination steps is described in this report along with the results of laboratory process test studies. In addition, the status of some of the more basic development work carried on concurrently with the process studies is presented. This supporting work has included further study of the fluorination step, some of the chemistry involved in the NaF decontamination process, and exploratory work on the corrosion problem.

2.0 DESCRIPTION OF PROCESS

The recommended flowsheet for the fused salt-volatility process (see Fig. 2.1) has the following features:

Fused Salt-Fluorination Step

1. A F_2/UF_4 mole ratio of 6/1 results in essentially complete UF_6 volatilization at 600°C. The volatilization is over 90% complete at a mole ratio of 3/1. If the fused salt contains an unusually high oxygen content (oxy-compounds) a compensatory amount of F_2 is needed.

2. The optimum fluorination period is probably about 2 hr. For a 10-kg batch of uranium a F_2 rate of 1.7 scfm is required. A higher flow rate over a shorter period would increase the F_2 efficiency at the expense of encountering excessive mechanical entrainment of the salt and a lower decontamination effectiveness. A lower flow rate would only lead to magnification of the corrosion problem.

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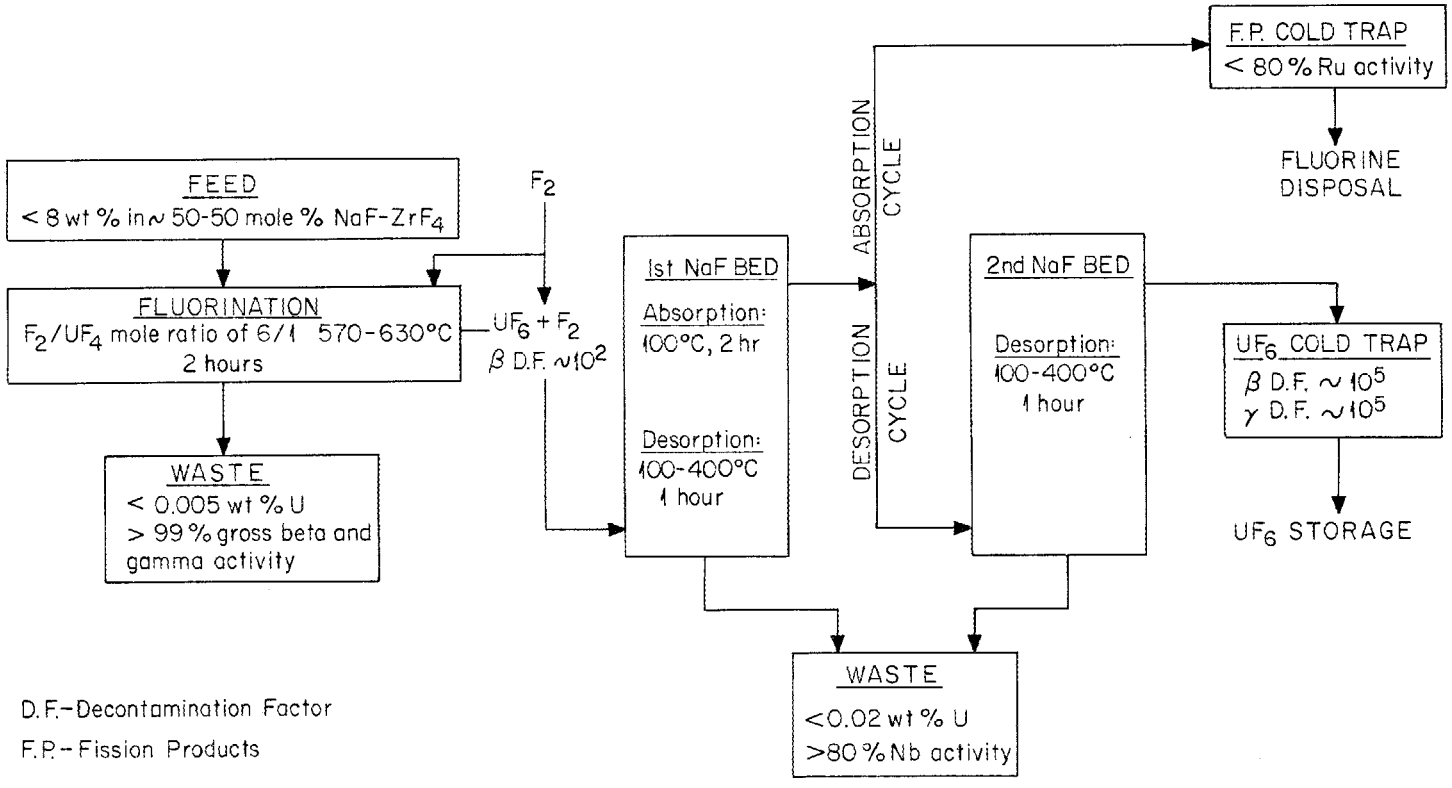


D.F.-Decontamination Factor

F.P.-Fission Products

Fig. 2.1. Flowsheet for Fused Salt-Fluoride Volatility Process.

NaF Absorption-Desorption Cycle

1. A NaF/U weight ratio (U being the total uranium being processed) of 2/1 to 3/1 is needed in each of the two NaF beds. The recommended grade of NaF is 12-20 mesh, prepared from pelletized material (Harshaw Chemical Company). The NaF beds should be preconditioned with a slow flow of F_2 for 1 hr at 400°C before process use.

2. The absorption cycle, using only the first bed, is carried out at approximately 100°C. Operation on a large scale will result in the bed temperature rising 50° or more due to heat of absorption. There is no reason why the temperature could not be closer to the triple point of UF_6 (65°C) initially to partly compensate for this effect.

3. Desorption of UF_6 from the first bed through the second bed requires about 1 hr, using the same F_2 flow rate employed in the absorption cycle. The desorption cycle consisted, in laboratory tests, of raising both NaF beds simultaneously from 100 to 400°C in about 0.5 hr, at which time the transfer of UF_6 to the cold trap system was essentially complete.

3.0 PROCESS DEVELOPMENT STUDIES

3.1 Fused Salt-Fluorination Work

3.1.1 Fluorine Efficiency

When fluorine is introduced into fused $NaF-ZrF_4-UF_4$, the uranium content drops sharply as the F_2/U mole ratio increases (Fig. 3.1). Fluorine utilization efficiency is highest when 90% or more of the UF_6 has been volatilized (Fig. 3.2). The efficiency decreases thereafter, with the F_2 acting essentially as a sweep gas. In an ideal case, the amount of UF_6 volatilized would be stoichiometrically equivalent to the amount of F_2 introduced up to a F_2/U mole ratio of 1, thereafter decreasing hyperbolically.

The F_2/U mole ratio required for volatilization of more than 99% of the UF_6 was decreased by the elimination of impurities, but it was not significantly affected by the concentration of uranium in the initial fused salt (Fig. 3.3).

Use of N_2 with the F_2, the method of gas introduction into the melt, and the rate of gas flow has some effect on the F_2/U mole

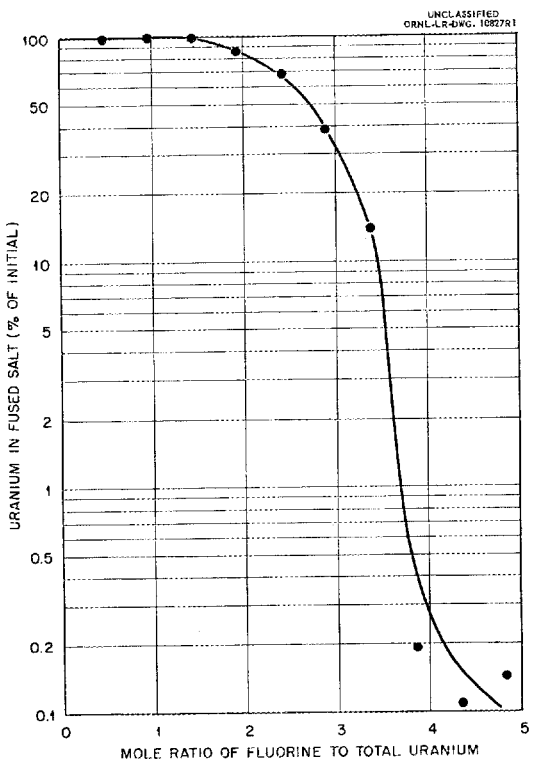


Fig. 3.1. Amount of UF_6 Remaining in 375 g of $NaF-ZrF_4-UF_4$ (50-46-4 mole%) Fluorinated at 600°C at a Rate of 100 ml/min as a Function of Amount of Fluorine Introduced.

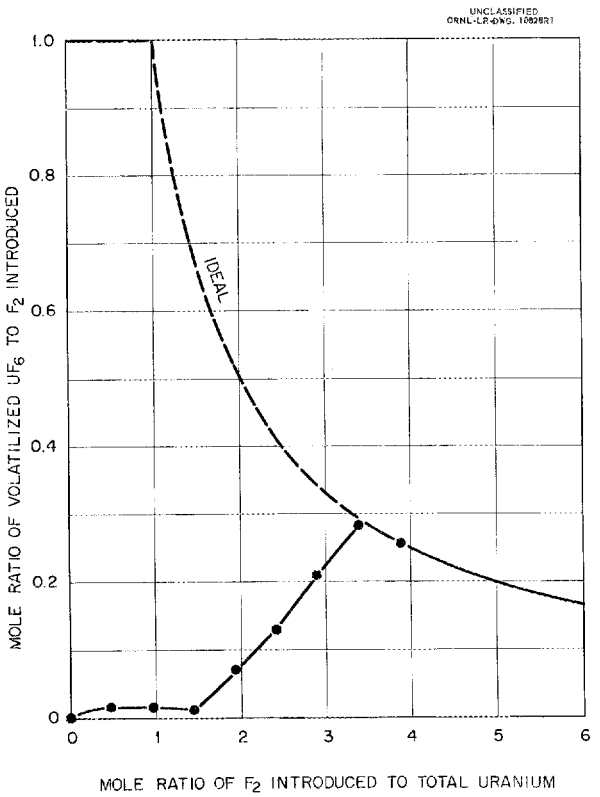
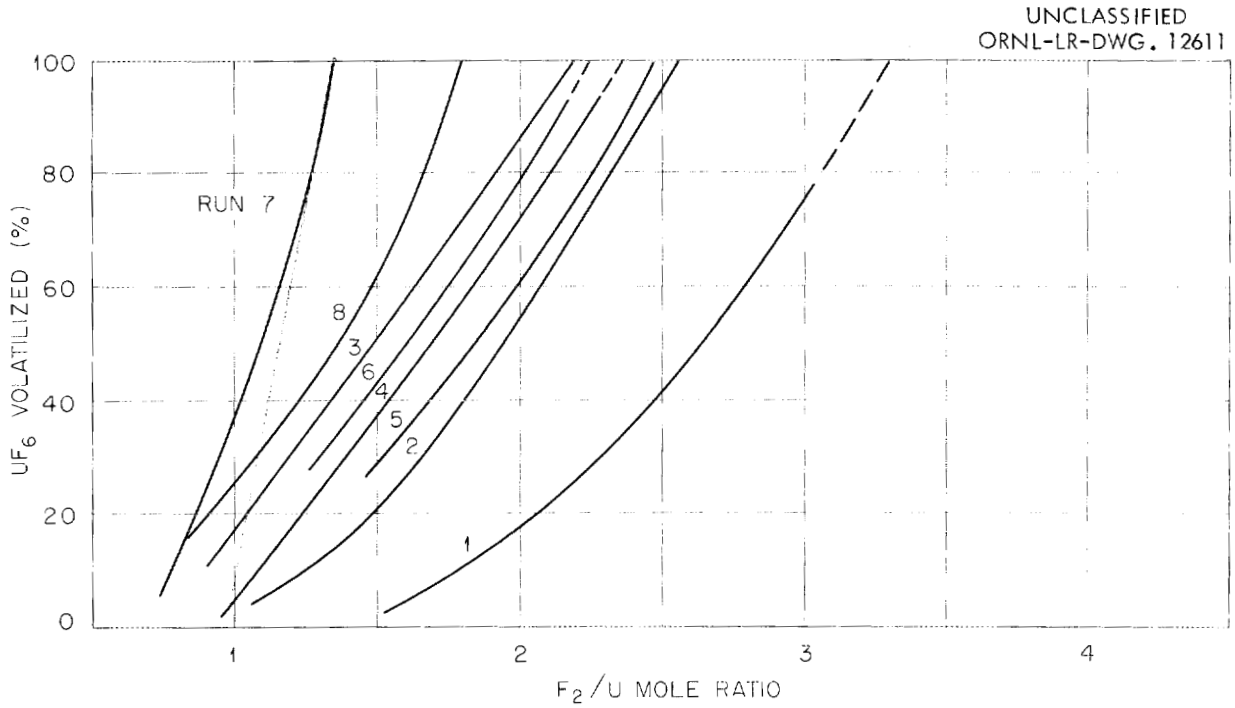


Fig. 3.2. Efficiency of UF_6 Volatilization as a Function of Amount of Fluorine Introduced.



RUN NO.	MOLTEN SALT	U CONTENT (mole %)
1	AS-RECEIVED $NaF-ZrF_4-UF_4$ (50-46-4 mole %)	4
6	$NaF-ZrF_4-UF_4$ (50-46-4 mole %), HYDROFLUORINATED 4 hr AT 600°C	4
7	PREFLUORINATED $NaF-ZrF_4$ (50/46 mole RATIO) PLUS UF_4 (76.2%* URANIUM)	4
8	PREFLUORINATED $NaF-ZrF_4$ (50/46 mole RATIO) PLUS UF_4 (76.2%* URANIUM); AIR-SPARGED FOR 2 hr BEFORE FLUORINATION	4
2	PREFLUORINATED $NaF-ZrF_4$ (50/46 mole RATIO) PLUS UF_4 (72.9%* URANIUM)	4
3	PREFLUORINATED $NaF-ZrF_4$ (50/46 mole RATIO) PLUS UF_4 (72.9%* URANIUM)	4
4	PREFLUORINATED $NaF-ZrF_4$ (50/46 mole RATIO) PLUS UF_4 (72.9%* URANIUM)	2
5	PREFLUORINATED $NaF-ZrF_4$ (50/46 mole RATIO) PLUS UF_4 (72.9%* URANIUM)	1

* THEORETICAL = 75.8%

Fig. 3.3. Effect of Uranium Concentration and Impurities of the Fused Salt Fuel Mixtures on the Fluorine-to-Uranium Mole Ratio Required for UF_6 Volatilization. Conditions: 100 ml of F_2 per min; 1/16-in.-dia sieve plate on dip tube that introduced fluorine to melt.

ratio, but the results could not be correlated with the known variables (Fig. 3.4).

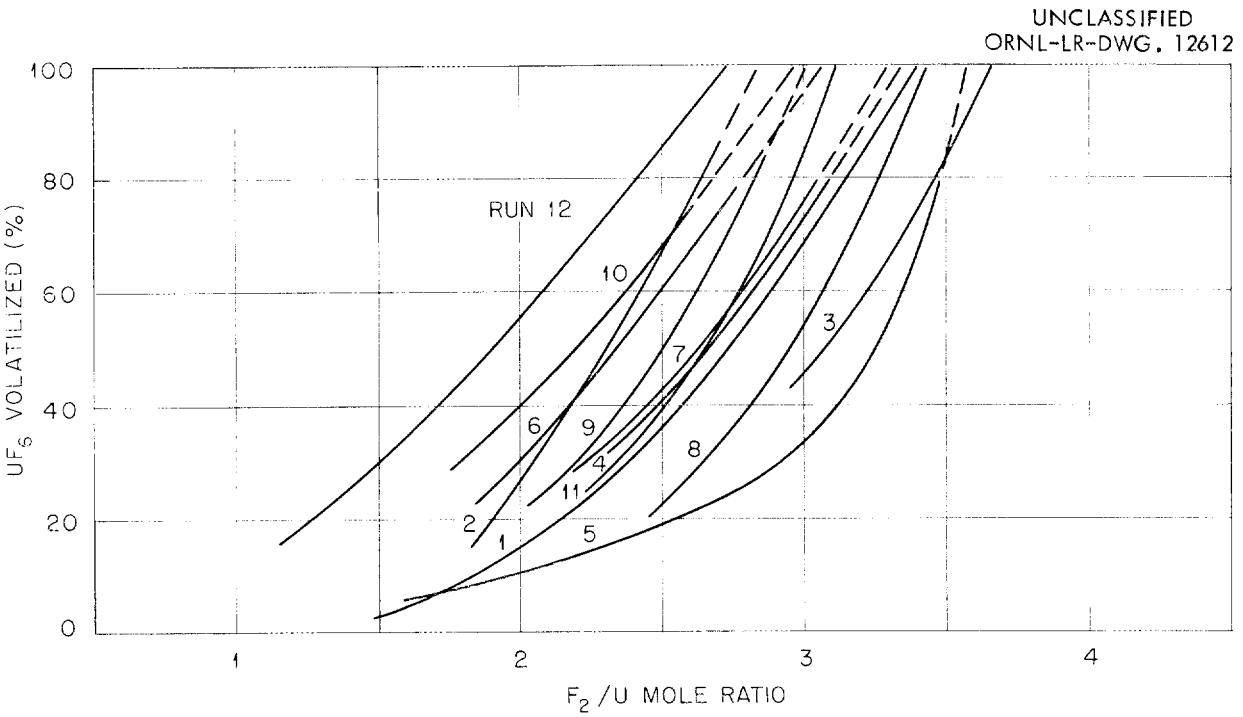
These experiments were performed at 600°C in a 2-in.-dia nickel reactor with a 375-g charge of $NaF-ZrF_4-UF_4$. In some of the tests the salt was made by the addition of UF_4 to $NaF-ZrF_4$ (50/46 mole ratio) that was believed to be relatively free of oxide impurities as a result of previous use in a fluorination run. Uranium tetrafluoride concentrations of 1, 2, and 4 mole % were used to study the effect of concentration. In other tests $NaF-ZrF_4-UF_4$ (50-46-4 mole %) was used as received. Data were obtained by direct sampling of the salt at intervals during the fluorination. The curves were extrapolated to the 100% volatilization point for comparison, but usually a sharp break was observed in the curve between 95 and 100%, which extended the curve to higher fluorine-to-uranium mole ratios for volatilization of the last traces of UF_6.

Volatilization of more than 99% of the UF_6 from as-received $NaF-ZrF_4-UF_4$ required a fluorine-to-uranium mole ratio of about 3.1/1, which was reduced to about 2.2/1 by sparging with HF for 4 hr before fluorination. In two tests with the fuel mixture synthesized by adding UF_4 with a uranium content of only 72.9% (theoretical, 75.8%) to prefluorinated $NaF-ZrF_4$, the fluorine-to-uranium mole ratio required for more than 99% UF_6 volatilization was about 2.4/1. When very pure UF_4, uranium assay of 76.2%, was used, the fluorine-to-uranium mole ratio was 1.4/1, which represents a fluorine utilization efficiency of about 70%.

A quick-freeze sampling technique was used in all of the fluorination work. A comparison of sampling methods showed that agreement to within 3% was obtained in uranium analyses of samples taken during the course of fluorination experiments with the use of a dip ladle, immersion of a solid rod into the fused salt to obtain a quick-freeze sample, and samples taken after fluorination by grinding and sampling the entire batch of salt. This study was made with three different uranium concentrations in the $NaF-ZrF_4$ salt, 8, 2, and 0.5 wt %.

3.1.2 Corrosion Studies

The corrosion of nickel test coupons and of a nickel vessel was fairly low after 20 fused salt-fluorination runs at 650°C, confirming previous work.[5] Since conditions changed continually during the runs and since the various components of the vessel were attacked to different degrees, a calculated over-all corrosion rate would have no significance. However, it appears that a large number of fluorination runs can be made in one reaction vessel before the



RUN NO.	FLOW RATE (ml/min) F_2	N_2	GAS DISPERSION DEVICE ON END OF $^1/_4$-in.-DIA DIP TUBE
10	100	0	NONE
5	40	200	SIEVE PLATE, $^3/_{64}$-in.-DIA HOLES
1	100	0	SIEVE PLATE, $^3/_{64}$-in.-DIA HOLES
2	100	200	SIEVE PLATE, $^3/_{64}$-in.-DIA HOLES
3	150	0	SIEVE PLATE, $^3/_{64}$-in.-DIA HOLES
4	150	150	SIEVE PLATE, $^3/_{64}$-in.-DIA HOLES
6	300	0	SIEVE PLATE, $^3/_{64}$-in.-DIA HOLES
7	100	0	SIEVE PLATE, $^1/_{16}$-in.-DIA HOLES
8	100	200	SIEVE PLATE, $^1/_{16}$-in.-DIA HOLES
9	150	0	SIEVE PLATE, $^1/_{16}$-in.-DIA HOLES
11	100	0	THREE SIEVE PLATES, $^3/_{64}$-in.-DIA HOLES, $^1/_2$ in. APART
12	100	0	PERCOLATOR DRAFT TUBE

Fig. 3.4. Effect of Sparge Gas Flow Rate and Method of Introduction of Fluorine into the Melt on UF_6 Volatilization.

corrosion is too severe. A summary of the resistance of various metals to fluorination conditions at high temperatures has been reported elsewhere.[3]

The "A" nickel reaction vessel was 2 in. in diameter. The three test coupons were mounted in an upright position at the bottom of the reaction vessel, as shown in Fig. 3.5, in such a way that one-third the surface area of each coupon extended from the liquid into the gas phase. The coupons were 3 in. long, 3/4 in. wide, and 1/4 in. thick. Two of the coupons were "A" nickel (nominal composition: 99.4% Ni, 0.05% C), and one of them was cut longitudinally and welded. The third coupon, which was "L" nickel (nominal composition: 99.4% Ni, 0.01% C), was also cut longitudinally and welded.

Each run was made with 200 g of $NaF-ZrF_4-UF_4$ (50-46-4 mole %). The time for a run varied from 4.58 to 0.83 hr, the reaction vessel and the coupons being exposed to process conditions for a total of 30 hr. The fluorine flow rate varied from 50 to 300 ml/min and was regulated so that 9.4 moles of fluorine was used per mole of uranium in each run.

Corrosion of the welded coupons (both "A" and "L" nickel) was somewhat greater than that of unwelded ones, but in both cases the corrosion was of the solution type (Fig. 3.6), and there was fairly uniform surface removal. Dimensional and weight-change analyses also showed that corrosion may have been slightly greater in welded than in unwelded coupons (Table 3.1). The most severe attack was on the outer surface of the fluorine gas inlet tube in the vapor zone (Fig. 3.7). It is very likely that this attack, about 2 in. above the salt surface, was due to the frequent admission of atmospheric moisture and oxygen into the reactor possibly producing an aqueous HF and oxidation attack when it was at an elevated temperature. The same type of attack did not occur at the reactor wall. Corrosion on the F_2 inlet tube in the liquid zone was more uniform and varied from 4.0 to 7.5 mils in depth. The reaction vessel showed nonuniform attack of 5 to 9 mils in both the liquid and gas zones; in the region in contact with molten salt the attack was of a solution nature (Fig. 3.8).

3.1.3 Recovery Yield of UF_6

Uranium hexafluoride recovery was more than 99.0% in the 20-run corrosion series (Sec. 3.1.2). The recovery of uranium was high in all runs (Table 3.2). The uranium loss in the waste salt was consistently lowest in the 50-min runs at the highest fluorine flow rate. This result was possibly due to a smaller loss of fluorine in corrosion

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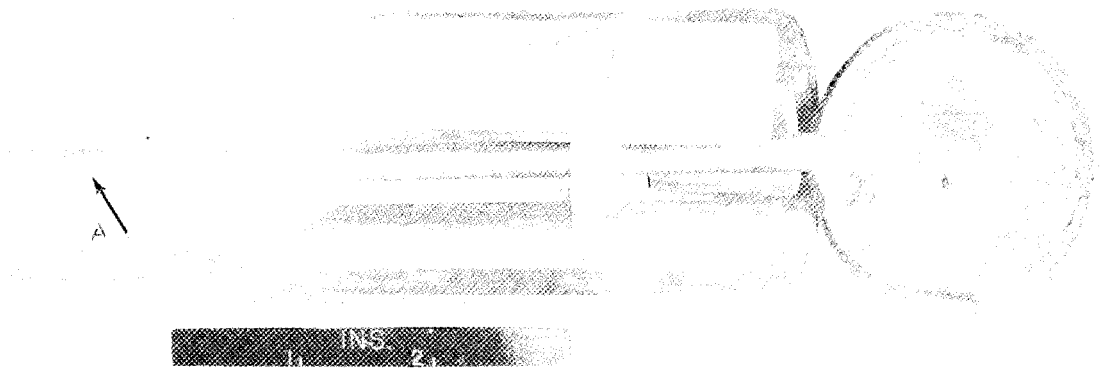

Fig. 3.5. Cross Section of Assembled "A" Nickel Reaction Vessel. The pitting on the fluorine gas inlet tube may be seen at point A.

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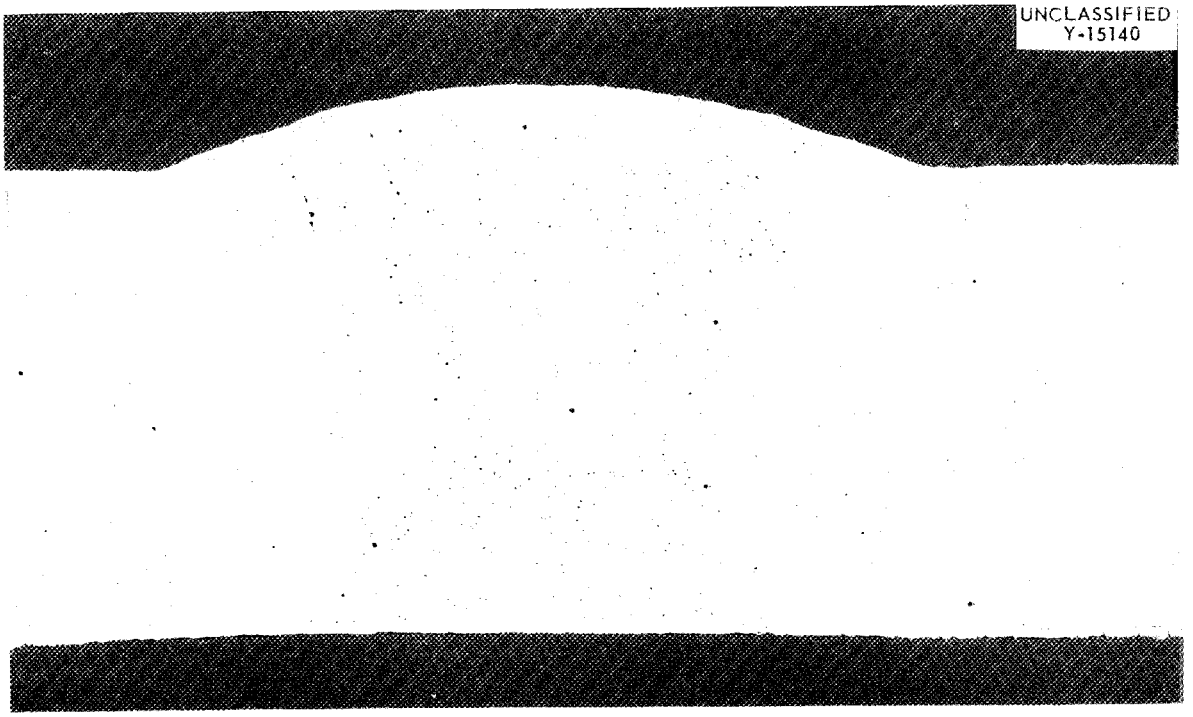

Fig. 3.6. Cross Section of Welded "L" Nickel Test Coupon Exposed to Molten Salt in a Nickel Reaction Vessel. Note uniformity of attack. Etched with KCN plus $(NH_4)_2S_2O_8$. 12X.

Table 3.1. Weight Loss of Nickel Corrosion Coupons Tested in Laboratory-Scale Fluorination Runs

Type of Coupon	Original Weight (g)	Final Weight (g)	Weight Change (g)	Weight Change (%)
Welded "L" nickel	83.9878	80.3760	3.6118	4.3
Welded "A" nickel	86.3445	82.7515	3.5930	4.2
Unwelded "A" nickel	82.6071	80.2160	2.3911	2.9

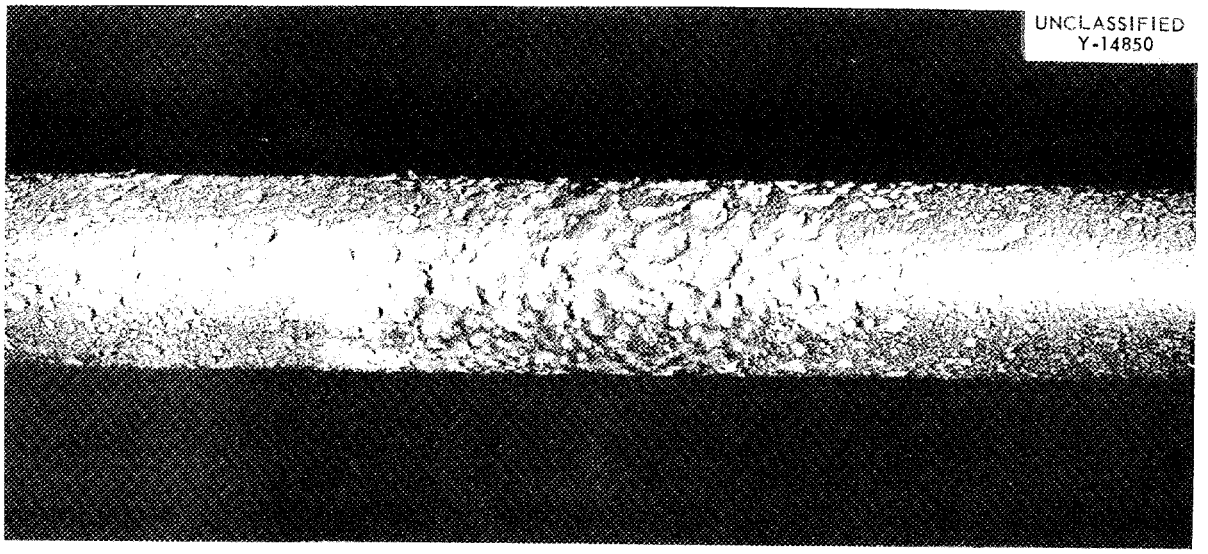

Fig. 3.7. Outer Surface Attack of Fluorine Gas Inlet Tube in Vapor Zone of Reaction Vessel. Section taken at point A of Fig. 3.5. Etched with KCN plus $(NH_4)_2S_2O_8$. 20X.

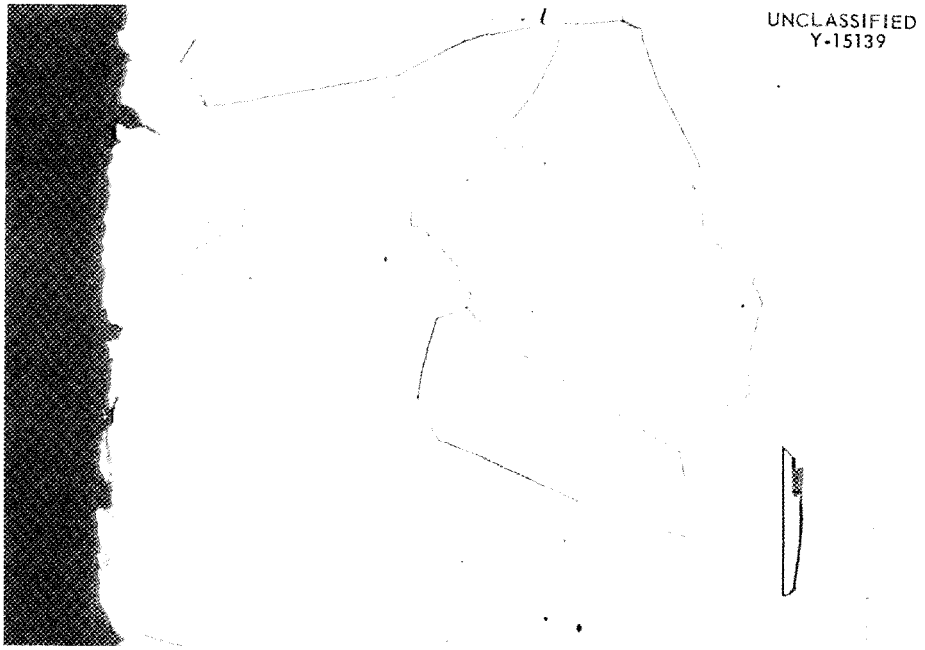

Fig. 3.8. Inner Surface of Specimen of "A" Nickel Reaction Vessel Taken From Region Exposed to $NaF-ZrF_4-UF_4$ Fuel. Note nonuniform surface attack. Etched with KCN plus $(NH_4)_2S_2O_8$. 250X.

in the short runs than in the long runs. Out of 3935 g of salt, 341 g of uranium was recovered as UF_6, which corresponds to an initial uranium content of 8.66%. Analyses of this batch of fuel ranged from 8.30 to 8.76% uranium. Even if the higher value is assumed, recovery was 99.0%.

3.1.4 Behavior of NiF_2 in Corrosion

The behavior of NiF_2 in molten $NaF-ZrF_4$ and $NaF-ZrF_4-UF_4$ systems was studied to determine if the presence of this corrosion product would form sludges which would interfere with salt transfers in the fluoride volatility process. Although NiF_2 has been reported to be fairly insoluble in this type of salt (approximately 0.2 wt % as Ni at 600°C), at higher concentrations NiF_2 readily forms a viscous dispersion which settles slowly. Based on this observation, it was concluded that NiF_2 concentrations up to 2 wt % would not interfere with salt transfers unless the molten salt were permitted to stand, unagitated, for long periods of time.

Anhydrous NiF_2 was added to molten $NaF-ZrF_4$ (50-50 mole %); the mix was heated until a clear solution was obtained and then cooled until turbidity reappeared. Solubility values (Table 3.3) estimated by the disappearance of turbidity were in fairly good agreement with those determined electrochemically on 53 mole % NaF-47% ZrF_4 salt.

Addition of as much as 6 wt % NiF_2 to molten $NaF-ZrF_4$ (50-50 mole %) at 600°C resulted in the formation of a viscous dispersion which was fairly stable. Although some settling of NiF_2 was evident after only 0.5 hr with an initial nickel concentration of 2 wt %, complete settling had not occurred even after 72 hr (Table 3.4). With 1 wt %, settling was more nearly complete at 72 hr since the NiF_2 concentration and viscosity at the bottom could not increase as much. The results for the $NaF-ZrF_4-UF_4$ system appear very similar to those for the uranium-free system (Table 3.5). However, with 2 wt % Ni and with uranium present the settling was less after 2 hr than in the test with no uranium. Since the solubility of NiF_2 is represented by the lower limit of nickel concentration encountered in the settling tests, it appears to be approximately the same in uranium-bearing and uranium-free salt.

The tests were made by dry mixing the required amount of salt (~ 30 g), and melting in a 1/2-in.-i.d. nickel tube. Nitrogen was used initially for agitation and then as a blanket while the material was kept at 600°C for various times. The tube was quickly quenched with cold water at the end of the test to fix the NiF_2 concentration at various heights in the tube. The tube was then cut into 1/2-in.-long sections and the salt was analyzed for nickel.

Table 3.2. Uranium Losses in Laboratory-Scale Fluorination Runs

Number of Runs	Duration (hr)	Fluorine Flow Rate (ml/min)	Uranium Loss in Waste (% of Total)
1	4.58	55	0.11
5	2.50	100	0.02 to 0.16
5	1.25	200	0.06 to 0.23
9	0.83	300	0.01 to 0.04

Table 3.3. Visual Determinations of Solubility of NiF_2 in $NaF-ZrF_4$ (50-50 mole %)

Temperature (°C)	Solubility (wt % NiF_2)
640	0.7
670	1.0
685	1.3

Table 3.4. Sedimentation of NiF_2 in Molten $NaZrF_5$

Temperature: 600°C

Relative Position of Sample	Ni Concentration (wt %)				
	Initial Content	After 0.5 hr	After 2 hr	After 8 hr	After 72 hr
Initial Ni Content[a] - 2 wt %					
1 (top)	1.60	---	0.28	0.20	---
2	1.74	0.73	0.30	0.22	0.20
3	1.72	1.72	2.20	1.40	0.21
4	1.78	1.86	2.62	3.48	1.23
5 (bottom)	2.13	2.02	3.02	3.54	2.99
Initial Ni Content[a] - 1 wt %					
1 (top)	---	---	---	---	0.22
2	---	---	0.30	---	0.16
3	---	---	0.31	---	0.17
4	---	---	1.71	---	0.18
5 (bottom)	---	---	3.06	---	---

[a]The nickel was added as NiF_2.

Table 3.5. Sedimentation of NiF_2 in Molten $NaF-ZrF_4-UF_4$ (48-48-4 mole %)

Temperature: 600°C

Relative Position of Sample	Ni Concentration (wt %)				
	Initial Ni, 2 wt %		Initial Ni, 1 wt %		Initial Ni, 0.5 wt %
	After 2 hr	After 48 hr	After 2 hr	After 48 hr	After 48 hr
1 (top)	1.26	---	---	---	---
2	1.23	0.25	0.36	0.18	0.24
3	2.12	0.34	0.40	0.20	0.33
4	2.78	2.75	2.53	0.47	0.22
5 (bottom)	2.81	6.94	3.08	---	0.85

3.2 NaF Decontamination Step

3.2.1 Operation in a Temperature Range of 100-400°C

The flowsheet (Fig. 2.1) for the volatility process provides for volatilizing UF_6 from molten fluoride salt with fluorine, absorbing the UF_6 on NaF at 100°C, then desorbing with fluorine at 100-400°C and passing the desorbed UF_6 through a second NaF bed to the final cold trap. In the case of long-decayed uranium reactor fuel, most of the volatile activity in the UF_6 stream from the molten salt step is due to ruthenium and niobium, both of which form volatile pentafluorides. Laboratory tests have demonstrated that ruthenium is not absorbed very much on NaF at 100°C, but effectively passes through the first NaF bed with the excess fluorine used in the molten salt step. Niobium, on the other hand, is absorbed on the NaF with the UF_6. This absorption is predominantly irreversible since the niobium remains for the most part with the NaF during UF_6 desorption. Use of the second NaF bed appears essential to prevent cross contamination and to achieve effective decontamination of the UF_6 (particularly from any ruthenium revolatilized from the end of the first bed) in processing consecutive batches. Much of the ruthenium remaining in the first NaF bed is "plated out" over all of the metal surface, including that near the outlet. This problem has also been encountered in distillation work.[4] The effective absorption of ruthenium activity on NaF at high temperatures (see Sec. 3.2.2) is perhaps partly responsible for the efficiency of the second bed.

In six tests of the double-bed procedure (using 20-40 g uranium), the activity of the product UF_6 was less than the UX_1-UX_2 activity normal in natural uranium. Four of the tests were made consecutively with the same 60-ml NaF beds and showed that the decontamination effectiveness of the system does not decrease with use (Table 3.6). The over-all beta- or gamma-decontamination factor in each of the six runs was no less than 10^5, with 10^2 being attributable to the fused salt-fluorination step[1] and 10^3 to the absorption-desorption process. The low product activity made calculation of specific decontamination factors impractical. The effectiveness of the double bed system was shown in the six tests by the distribution of the volatilized activity (Table 3.7).

An over-all beta- or gamma-decontamination factor of greater than 10^4 was obtained by the absorption-desorption procedure using 200 ml NaF in a single bed (Table 3.8). Calculation of specific decontamination factors was possible because the product UF_6 was radioactive in excess of the UX_1-UX_2 level. The typical behavior of the ruthenium and niobium activities was also observed in this run.

Table 3.6. Summary of Four Consecutive Runs in Two-Bed Fused Salt Fluoride-Volatility Process

Conditions: 128 g of uranium in $NaF-ZrF_4-UF_4$ (52-44-4 mole %) with gross beta activity per milligram of uranium of 5×10^5 counts/min. Each run fluorinated with 1/1 F_2-N_2 mixture for 1.5 hr and then with pure F_2 for 0.5 hr; UF_6 in F_2-N_2 gas stream absorbed on NaF; UF_6 desorbed at 100-400°C through second NaF bed into a cold trap

Average F_2/U mole ratio in absorption period: 4/1

Average F_2/U mole ratio in desorption period: 2/1

Absorbent beds: 60 ml of 12- to 40-mesh NaF in 1-in.-dia tubes

NaF/U weight ratio after four runs: 1/1

Run	Product Yield (%)	Uranium Retention (%)				Product Gamma Activity per Milligram of Uranium[a] (cts/min)
		First Cold Trap	First NaF Bed	Second NaF Bed	Waste Salt	
1	83	0.01			0.02	3.6
2	35.2	0.10			0.05	3.1
3	151	0.07			0.08	1.0
4	43.8	0.08			0.02	2.1
Over-all	70.1	0.06	0.5	5.1	0.04	2.5

[a]Gamma activity per milligram of natural uranium is 8 cts/min.

Table 3.7. Distribution of Volatilized Activity in the Two-Bed NaF Procedure

Runs 1, 2, 3, and 4: Consecutive tests with two 60-ml NaF beds (12-40 mesh) in 1-in.-dia tubes. Total NaF/U weight ratio for both beds in each run: 4/1. NaF/U ratio over four runs: 1/1

Runs 5 and 6: Single-batch runs with two 90-ml NaF beds (12-40 mesh) in 1-in.-dia tubes. Total NaF/U weight ratio for both beds: 6/1

	Percent of Total Volatilized Activity								
	Runs 1, 2, 3, and 4			Run 5			Run 6		
Activity	Fission Product Cold Trap	First NaF Bed	Second NaF Bed	Fission Product Cold Trap	First NaF Bed	Second NaF Bed	Fission Product Cold Trap	First NaF Bed	Second NaF Bed
Gross beta	81	18	0.85	51	48	0.8	59	24	17
Gross gamma	11	89	0.14	3	97	0.07	7	93	0.02
Ru gamma	97	1.6	1.1	81	18	0.9	86	14	Very low
Zr-Nb gamma	2.2	98	0.04	0.4	~100	0.04	0.8	99	0.02
Total rare-earth beta	4.3	92	3.6	3	97	0.1	3	97	Very low

Table 3.8. Decontamination of UF_6 in the Single-Bed Fused Salt Fluoride-Volatility Process

UF_6 in F_2-N_2 gas stream from fluorination of NaF-ZrF_4-UF_4 (gross beta activity per milligram of uranium in salt = 5×10^5 cts/min) at 600°C; absorbed on NaF at 100°C, desorbed with excess F_2 by increasing the temperature from 100 to 400°C

Absorbent: 200 ml of 12- to 40-mesh NaF in 1-in.-dia bed

Total F_2/U mole ratio: ~ 5

NaF/U weight ratio: ~ 6

Product yield: 87%

Activity	Decontamination Factors		
	Absorption[a]	Desorption[b]	Over-all, Including Fluorination
Gross beta	2.1	40	1.2×10^4
Gross gamma	1.2	310	1.4×10^4
Ru gamma	2.4	46	1100
Zr-Nb gamma	1.0	1600	5.9×10^4
Total rare-earth beta	1.0	5	

[a]Based on activity not absorbed with UF_6 on NaF but passed into cold trap.

[b]Based on activity remaining on NaF after desorption of UF_6.

The uranium retention on the two NaF beds in the four-run series was respectively 0.5 and 5.1% (Table 3.6). This excessive loss was due to some back-pressure buildup, which was evident in all runs, as the result of either partial plugging of the NaF beds or a stoppage in the UF_6 cold trap. It is essential to avoid any prolonged restriction of the gas flow, which would result in a major part of the UF_6 remaining in the bed as it approaches 400°C (see discussion of decomposition effect, Sec. 4.3). For example, three successive complete cycles with UF_6 in a two-bed NaF system, where little plugging occurred, resulted in retentions of 0.04 and 0.01%, respectively, in the two beds. In a single-cycle test with the same equipment, the uranium retentions were 0.05 and 0.01% respectively. The per cent of loss, therefore, does not appear to depend on the number of cycles.

3.2.2 Operation at a Temperature Above 600°C

Fair decontamination was obtained with NaF in either a 9- or an 18-in.-long bed at 650°C when the NaF/U weight ratio was 3/1 (Table 3.9, Runs 1, 2, 3) or 6/1 (Table 3.10, Runs 1 and 3). When the 9-in.-long bed was re-used (Table 3.9, Runs 3 and 4), so that the over-all NaF/U weight ratio was 1.5/1 for both runs, decontamination factors for gross beta, gross gamma, and ruthenium beta decreased sharply. With the 18-in.-long bed the same effect was observed, although here the over-all NaF/U weight ratio for the two runs was 3/1 (Table 3.10, Runs 1-2 and 3-4). The imperfect decontamination of the UF_6 in any single run and the ruthenium absorbed in one run leads to cross-contamination over consecutive runs (illustrated by sharp decrease in ruthenium gamma-decontamination factors in subsequent runs). However, the high effectiveness of NaF in removing ruthenium at > 600°C was in contrast to the much smaller effect observed in a UF_6 absorption cycle at 100°C (see Sec. 3.2.1).

Use of NaF at 600-650°C was discontinued because of the excessive corrosion, the difficulty with which the temperature was maintained, and the great variation of uranium retention on the bed. The best results were secured with a high flow rate for the UF_6-F_2 gas stream from the molten salt step. When the flow rate was decreased in order to secure more decontamination, the uranium retention became very high (see Sec. 4.3). Actual sintering of the NaF bed usually occurred at high uranium retentions, thus accounting for some of the excessive corrosion.

Table 3.9. Decontamination in a 9-in.-long NaF Absorbent Bed

UF_6-F_2 gas stream from fluorination of NaF-ZrF_4-UF_4 (52-44-4 mole %) fuel at 600 to 650°C passed through 1-in.-dia NaF bed (12-40 mesh) with temperature of 650°C in hottest portion; same bed used in Runs 3 and 4

F_2/U mole ratio: Run 1 - 3.7 Run 3 - 8.2
Run 2 - 3.6 Run 4 - 4.8

NaF/U weight ratio in absorber: 3/1 for Runs 1, 2, and 3; over-all ratio for Runs 3 and 4 = 1.5/1

Activity	Decontamination Factors			
	Run 1	Run 2	Run 3	Run 4
	Over-all			
Gross beta	1.3×10^4	5800	1.0×10^4	2900
Gross gamma	3.2×10^4	2.1×10^4	2.4×10^4	4500
Ru gamma	1700	1600	1.0×10^4	200
Zr-Nb gamma	3.2×10^5	7.4×10^4	7.0×10^4	1.0×10^5
Total rare-earth beta	5.2×10^5	5.0×10^4	4.9×10^4	1.1×10^7
	Across Absorbent[a]			
Gross beta	340	200		35
Gross gamma	930	4100		220
Ru gamma	940	1400		62
Zr-Nb gamma	900	1.2×10^4		2000
Total rare-earth beta	8	17		8

[a]Calculated on basis of activity found in absorbent and final product.

Table 3.10. Decontamination in an 18-in.-long NaF Absorbent Bed

UF_6-F_2 gas stream from fluorination of NaF-ZrF_4-UF_4 (52-44-4 mole %) fuel at 600°C passed through 1-in.-dia NaF bed (12-40 mesh) with hottest point at 670°C; same bed used in Runs 1 and 2 and in Runs 3 and 4

F_2/U mole ratio: Run 1 - 8.1 Run 3 - 8.4
Run 2 - 9.9 Run 4 - 10.2

NaF/U weight ratio in absorber: 6/1 for Runs 1 and 3; over-all ratio for Runs 1 and 2 and Runs 3 and 4 was 3/1

Activity	Decontamination Factors			
	Run 1	Run 2	Run 3	Run 4
		Over-all		
Gross beta	3900	1600	4300	2400
Gross gamma	9700	2700	2.0×10^4	4000
Ru gamma	1500	140	6700	450
Zr-Nb gamma	3.5×10^4	2.9×10^4	9.8×10^4	5.2×10^4
Total rare-earth beta	3.7×10^4	1.0×10^5		
		Across Absorbent[a]		
Gross beta		2		14
Gross gamma		40		82
Ru gamma		5		31
Zr-Nb gamma		250		700

[a]Calculated on basis of activity found in absorbent and final product.

4.0 BASIC CHEMICAL STUDIES

4.1 NaF Capacity for UF_6

The absorption capacity of NaF for UF_6 was about 0.9 g of uranium per gram of salt for one lot of Harshaw Chemical Company material under a variety of conditions (Table 4.1). The capacity of Baker and Adamson Company reagent-grade NaF was 1.89 g of uranium per gram of salt. Absorption of UF_6 on NaF under an initial vacuum indicated a capacity range of 0.80 to 0.90 for different mesh sizes, while absorption values obtained when the excess UF_6 was removed with fluorine as a sweep gas varied from 0.72 to 0.86. Practically the same capacity values were obtained at 70, 100, and 150°C and at two different pressures. The capacity of 0.9 for the Harshaw Chemical Company material is independent of the particle size to which it is degraded. The 1.89 value for the capacity of the Baker and Adamson Company material corresponds closely to the molecular ratio in the complex $UF_6 \cdot 3NaF$. A complex of this nature has been reported by other investigators.[6]

As indicated, the original 1/8-in. pellets (Harshaw Chemical Company) had practically the same capacity as the same material degraded to 12-40 mesh. Examination showed that the lemon-yellow color, characteristic of the complex, was uniform inside the pellet. Although the material was therefore fairly porous, the limited capacity of approximately 47% of theoretical and a surface area of only about 1 m^2 per gram indicated that the crystallite size was about 10^3 angstroms. Severe conditioning of the NaF, such as heating to 100-400°C with either vacuum or an atmosphere of fluorine to eliminate HF or moisture, did not affect the capacity measurements. Weight-loss tests after prolonged heating showed that the HF or moisture content was no more than 0.05%.

4.2 Pressure of UF_6 Above $UF_6 \cdot 3NaF$ Complex

Vapor-pressure data for the UF_6-NaF complex were obtained by the transpiration method over the temperature range 80 to 320°C (see Fig. 4.1). The reaction involved is described by the equation

$$UF_6 \cdot 3NaF(s) \longrightarrow UF_6(g) + 3NaF(s). \qquad (1)$$

The data are fitted with the analytical expression

$$\log P_{mm\ Hg} = 10.88 - (5.09 \times 10^3/T),$$

Table 4.1. Absorption Capacity of NaF for UF_6

Material	Conditions			Capacity (g of U per g of NaF)
	UF_6 Pressure (psia)	Temp. (°C)	Removal of Excess UF_6	
	Harshaw Chemical Co.			
12 to 40 mesh	15[a]	100	Not removed	0.86
	15[a]	100	By vacuum	0.86
	7.5[a]	100	By vacuum	0.80
	15[a]	70	By vacuum	0.88
	15[a]	150	By vacuum	0.90
	15[a]	100	By fluorine	0.86
	15[b]	100	By fluorine	0.86
8 to 12 mesh	15[b]	100	By fluorine	0.81
1/8-in. pellets	15[b]	100	By fluorine	0.72
	15[a]	100	By vacuum	0.81
	Baker and Adamson Co.			
Powder	15[a]	100	By vacuum	1.89

[a] UF_6 introduced to NaF under vacuum.

[b] UF_6 introduced at atmospheric pressure to displace fluorine.

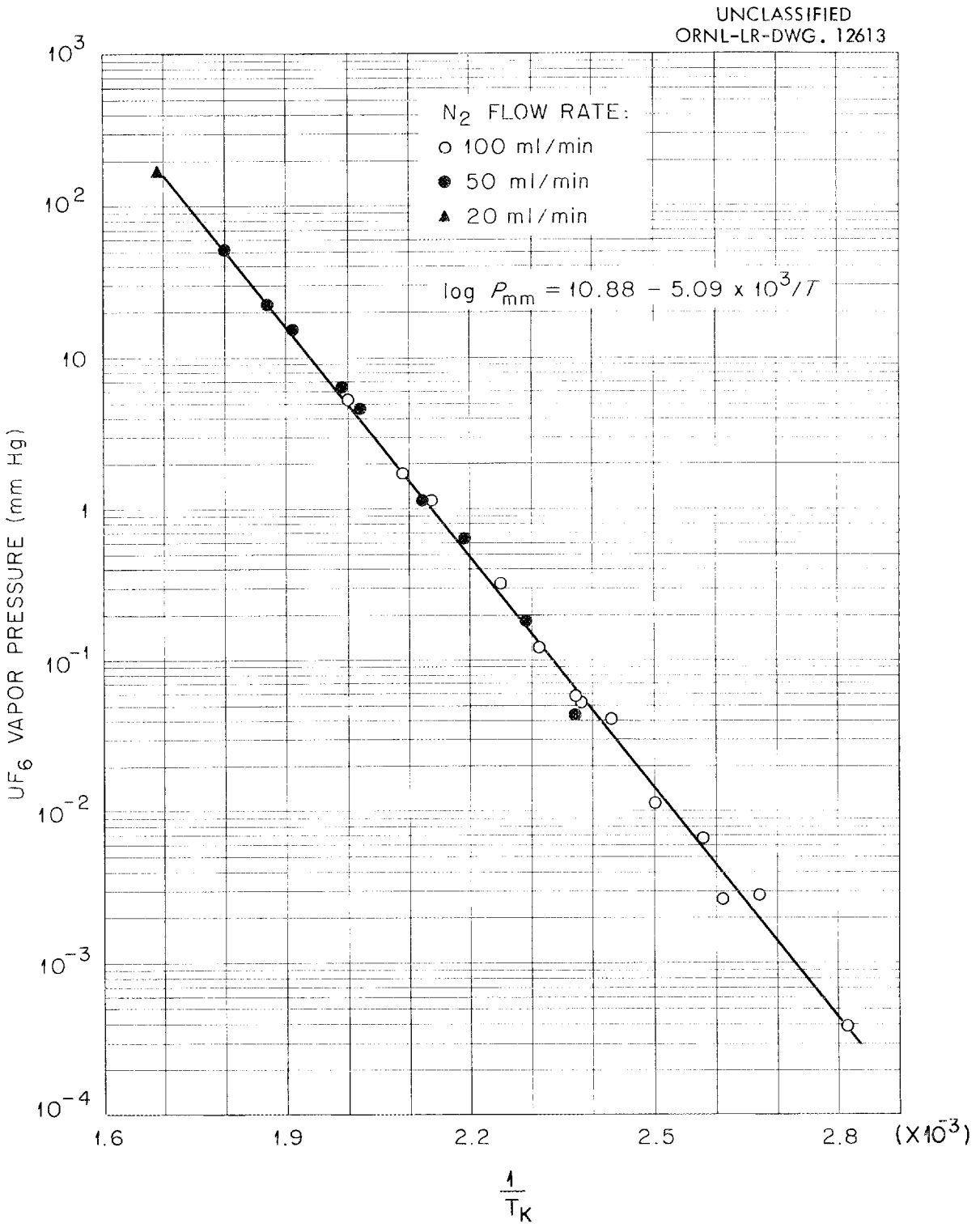

Fig. 4.1. Dependence of UF_6-NaF Complex Vapor Pressure on Temperature.

where T is the absolute temperature. Use of the Clausius-Clapeyron formula with this equation gave a value of +23.2 kcal per mole of UF_6 for the enthalpy change of Eq. 1.

The data were obtained by passing nitrogen at a flow rate of 100 ml/min, or less, through a prepared bed of the UF_6-NaF complex at any desired temperature, trapping out the UF_6 in the nitrogen stream in a dilute $Al(NO_3)_3$ solution, and measuring the total volume of nitrogen with a wet-test meter. The UF_6 hydrolysis samples were analyzed by colorimetric or fluorimetric methods to an accuracy of better than $\pm 5\%$. Temperature control of the bed was maintained always to within $\pm 0.2^{\circ}C$. The UF_6-NaF complex was prepared by saturating a 30-g bed of 12-20 mesh Harshaw NaF in a 1-in.-dia vertical nickel reactor with UF_6 at $100^{\circ}C$. Over 90% of bed saturation was maintained throughout the tests. Check runs, made at various N_2 flow rates, showed no flow-rate effect.

Crude adiabatic experiments were made with 100-ml batches of NaF to show that the reaction heat of 23.2 kcal per mole of UF_6 produces a large temperature rise, approximately $130^{\circ}C$, if total saturation with UF_6 (preheated to about $100^{\circ}C$) is carried out quickly in a period of a few minutes.

4.3 Decomposition of $UF_6 \cdot 3NaF$ Complex

A study of the decomposition of the $UF_6 \cdot 3NaF$ complex at temperatures of $245^{\circ}C$ and higher has confirmed the belief that uranium retention on the NaF bed will be excessive in the NaF desorption step if the temperature and sweep-gas flow rate are not properly controlled. The retention results from decomposition of the $UF_6 \cdot 3NaF$ complex to a complex of NaF with UF_5, which is not volatile.[5] A maximum decomposition rate of about 0.01, 0.09, and 0.5% per minute is incurred at 250, 300, and $350^{\circ}C$, respectively, in the absence of fluorine if all the uranium is assumed to be in the form of the solid complex $UF_6 \cdot 3NaF$. Under optimum conditions, UF_6 desorption from the NaF bed (see Secs. 3.1.1 and 4.2) competes favorably with the decomposition effect, resulting in a small uranium loss.

Fluorine appears essential to inhibit the decomposition reaction, and possibly to promote refluorination of the nonvolatile U(V) compound, formed in the decomposition. The possibility of any uranium retention by the decomposition mechanism in the absorption step at $100^{\circ}C$ appears to be insignificant, even over extended periods.

The temperature-dependence of the rate of decomposition of $UF_6 \cdot 3NaF$ was determined in a series of runs over the temperature

range 245-355°C (Fig. 4.2). The probable reaction involved is

$$UF_6 \cdot 3NaF \text{ (solid)} \longrightarrow UF_5 \cdot xNaF \text{ (solid)} + 0.5F_2 \text{ (gas)}.$$

The dependence of decomposition rate on temperature is

$$\log r = 6.09 - 5.22 \times 10^3/T$$

where r is the fractional decomposition rate in reciprocal minutes and T is the absolute temperature. The rate was calculated on the basis of an absorption capacity of 1.33 g of UF_6 per gram of NaF. The energy of activation was calculated as +23.9 kcal/mole of $UF_6 \cdot 3NaF$ complex. It is possibly significant that this energy change is approximately the same as the enthalpy change of +23.2 kcal per mole involved in the volatilization of UF_6 from the $UF_6 \cdot 3NaF$ complex.

The decomposition data were obtained with 4- to 5-g samples of NaF (Harshaw Chemical Company pellets classified to 12-20 mesh) held in a U tube (1/2-in.-dia stainless steel tubing), through which gaseous UF_6 was passed at atmospheric pressure. An oil bath was used for manually controlling the temperature to ±3°C during the course of each experiment. The runs were ended by removing the oil bath and rapidly cooling the sample. The $UF_6 \cdot 3NaF$ was formed at the beginning by saturating the NaF at a high UF_6 flow rate, after which the flow rate was decreased to 0.1-1 g/min for the remaining time. The length of the runs at various temperatures was adjusted so as to obtain a U(V) content in the final product of 1 to 10%. The excess UF_6 still absorbed on the NaF at the end of each test was not desorbed because of the difficulty of achieving this without increasing the U(V) content. The amount of $UF_6 \cdot 3NaF$ complex affected by the reaction was determined from U(V) and U(VI) analyses. A temperature above 355°C was not used since it would be difficult to maintain saturation of the NaF with UF_6 without use of a pressurized system.

In preliminary work on the decomposition reaction, a U(V) content of 20-26% represented a limit which could not be exceeded in one cycle of saturation of the NaF with UF_6 at 100°C followed by heating as a closed system to 350-400°C. Generally, in these runs, the NaF weight increase verified the assumption that the decomposition product is a complex of UF_5 with NaF. X-ray crystallography data indicated that the $UF_5 \cdot xNaF$ complex in the decomposition product has an orthorhombic structure with cell dimensions $a_0 = 4.90$ Å, $b_0 = 5.47$ Å, $c_0 = 3.87$ Å. The x-ray pattern of γ- or β-UF_5 was not observed in the material.

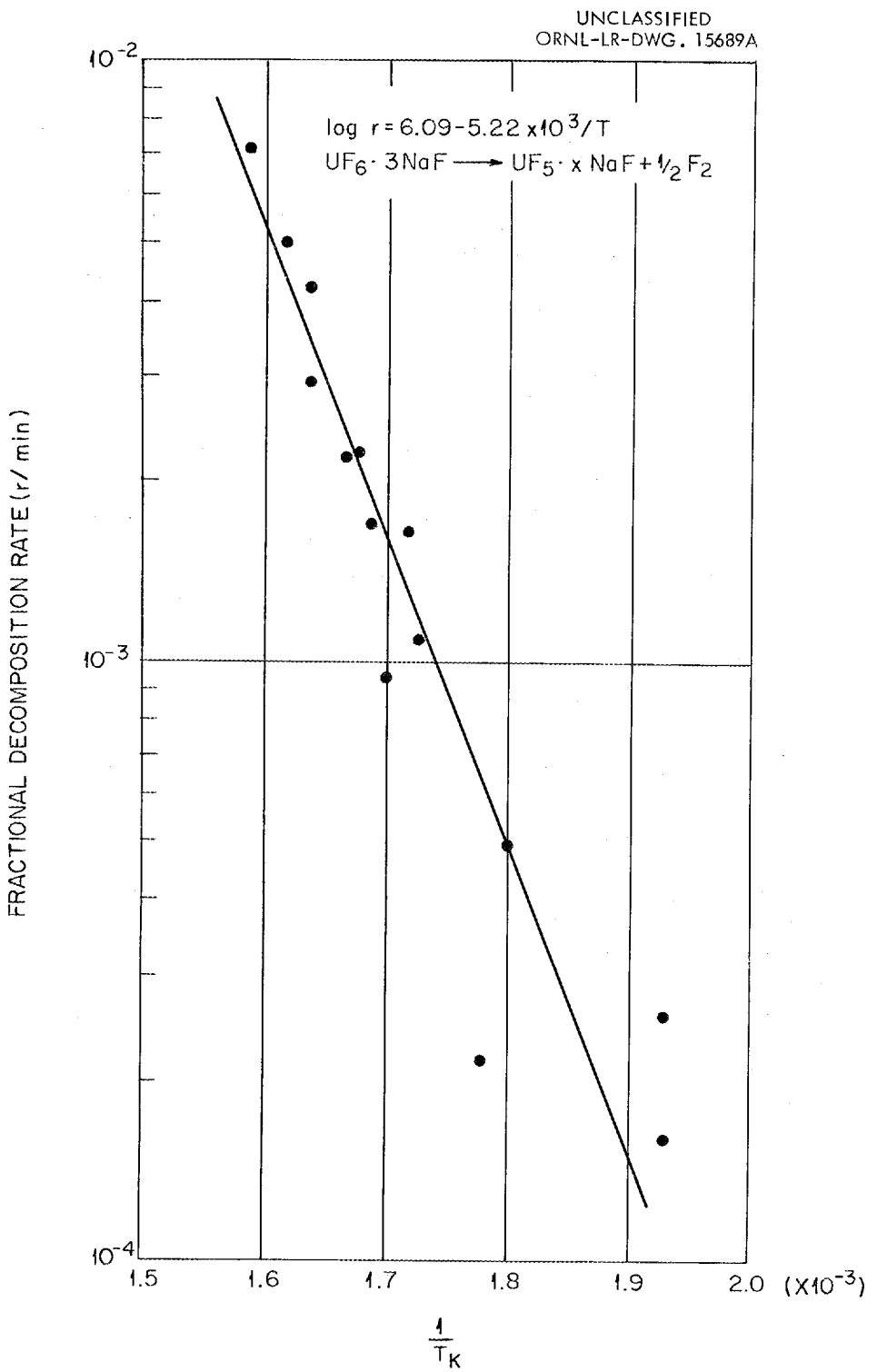

Fig. 4.2. Dependence of Rate of $UF_6 \cdot 3NaF$ Complex Decomposition on Temperature.

5.0 RECOMMENDATIONS

Both the fused salt-fluorination and NaF-absorption steps of the volatility process require further research and development. The presented laboratory studies have demonstrated the chemical feasibility of the process. Much further work will be needed, however, in adapting the process for use at the pilot-plant level. Chemical-engineering requirements will doubtless be a major factor in future modification of the process for use with various types of reactor fuel. Continued research is also essential to securing a better understanding of the basic chemistry involved in the two steps of the volatility process.

In the NaF absorption step, there is particular need of research on the behavior of NaF with various volatile fission-product fluorides. It seems quite likely, for example, that NaF has a high capacity with respect to the fluorides of zirconium and niobium due to the formation of definite chemical complexes. This would make renewal of the NaF beds possibly more economical than regeneration. On the other hand, the volatile fluorides of other fission products, such as Mo, Te, and I, may behave similarly to RuF_5 which apparently does not form a complex except at much higher temperatures.

The NaF method of decontaminating UF_6 from fission-product activity is potentially useful in many diverse forms. Although the decontamination factor of 10^5 (for the entire process) probably does not represent the top limit obtainable, use of a third bed should be considered if the double-bed system does not give the decontamination necessary with high-burn-up reactor fuels. It seems quite possible also that the multiple-bed system could be replaced with a single bed, either moving or fixed, used in conjunction with a thermal gradient. Much development work on the optimum physical structure of the NaF is needed. A suggested modification is the use of NaF structurally supported in some manner, either with metal (Ni) or a diluent material such as CaF_2 or AlF_3.

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