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ORNL - TM-752

Date - January 9, 1964

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RESULTS OF VOLATILITY PILOT PLANT COLD URANIUM FLOWSHEET DEMONSTRATION RUN TU-I

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ABSTRACT

A two element dissolution of 50.89 Kg of Zr-U alloy fuel element with 92 g/min of anhydrous HF in NaF-LiF-ZrF4 fused salt at 490 to 670° C was made with the fuel element 113% submerged. Initial and final ZrF_4 contents in the equimolar NaF-LiF fused salt were 25.1 and 40.3 mole %, respectively. Fluorination of the dissolver salt was accomplished with 12 SLM fluorine flow at 500-505° C. The sorption-desorption cycle of UF_6 on NaF was accomplished at 100°C and 100-400°C, respectively, in two fixed bed absorbers. Product UF_6 was collected in a cold trap.

A complete uranium material balance over the run was not made. However, non-recoverable uranium losses for the run were only 0.362g. Product impurity level was <1421 ppm total cations based on UF_6 with Na at 1300 ppm being the major impurity. A fuel dissolution rate of 2.52 Kg/hr was obtained with an over-all HF utilization of 35.2%. Fluorine utilization was 5.7% for 99.90% conversion of the UF_4 to UF_6. Final salt U content was 1.2 ppm. Fluoride Salt recovery was 100.5%. The generation of ~ 300g of off-gas solids occurred during dissolution.

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1.0 INTRODUCTION

The Volatility Pilot Plant is currently performing complete flowsheet demonstration runs with nonirradiated Zr-U alloy fuel elements. The purpose of this report is to disseminate the results of the first cold uranium flowsheet demonstration run, TU-1.

The ORNL Fluoride Volatility Pilot Plant was recently modified to process Zr-U alloy fuel elements. The principal modification was the addition of HF dissolution, or head-end, equipment to the ARE Pilot Plant facility. Dissolution of the fuel elements is performed with anhydrous HF in a molten salt of equimolar NaF-LiF containing 25-45 mole % ZrF_4 at 650-500°C. After dissolution, the UF_4 is converted to UF_6 by fluorination at 500°C, with subsequent decontamination from fission products during hot runs accomplished by an absorption-desorption cycle on NaF at 100°C and 100-400°C, respectively. Product UF_6 is collected in cold traps.

A series of equipment shakedown runs has been performed in the VPP to evaluate the performance of the head-end equipment (HF dissolution) for processing box-type fuel elements. Also, a series of seven development runs using dummy Zr-2 fuel elements has recently been performed. Currently, a series of flowsheet demonstration runs is progressing using nonirradiated uranium-bearing fuel elements for the dissolution studies.

Fig. 1 represents a schematic diagram of the entire Volatility Pilot Plant Flowsheet. In addition to accumulating additional data on fuel element dissolutions, the flowsheet demonstration runs are also designed to evaluate the fluorination step and the absorption-desorption cycle since both operations are performed in vessels of new geometry. Following completion of system containment and certain equipment modifications, processing of long cooled Zr-U fuel elements will commence.

2.0 PURPOSE

Run TU-1 was a complete flowsheet demonstration of the Volatility Process. In addition to the evaluation of the main process operations, that is hydrofluorination and fluorination, the purpose of the flowsheet demonstration run was to study and evaluate subsidiary operations and new process systems such as the dissolver off-gas filtration system. The ultimate objective of the runs in the cold uranium flowsheet demonstration

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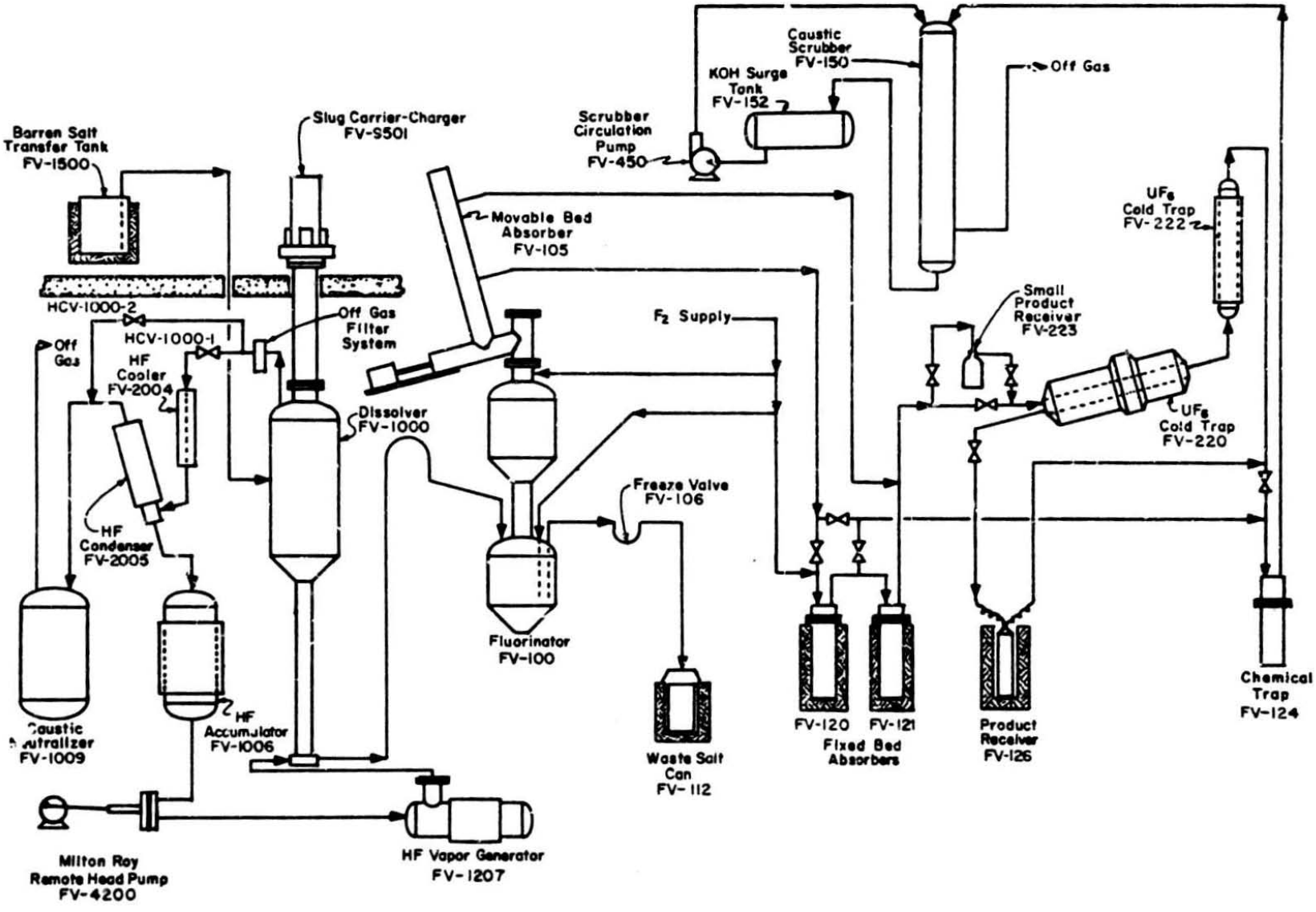

Fig. 1. Schematic diagram of Volatility Pilot Plant

series is to establish firm operating conditions for the VPP prior to the start of hot operations on long cooled Zr-U alloy fuels.

3.0 URANIUM PRODUCT

The uranium product, approximately 700-900 g as UF_6, from each of the cold runs is scheduled for collection in 4-in ID product cylinders to permit sampling of each run. Under normal operating conditions only a limited quantity of UF_6 is expected to pass the primary cold trap (FV-223, Fig. 1) and be retained in the secondary cold traps, FV-220 and FV-222. Material passing FV-223 will not normally be thermally transferred back to FV-223, and, therefore, a complete uranium material balance on each individual run will not be made. A complete material balance over the cold runs will be attempted when product is transferred to standard shipping cylinders. However, a water wash of the system will not necessarily be made at that time. Sampling of individual product cylinders will be primarily for the evaluation of chemical contaminants in the product during cold runs, and chemical and radiochemical contaminants during hot runs. All product from the cold runs will eventually be combined into two standard 5-in ID UF_6 product cylinders for shipment to the Y-12 Product Processing Department for uranium recovery. SS accountability for these transfers will be based on multiple sampling of the standard cylinders.[1]

3.1 Chemical Contaminants

3.1.1 Hydrofluoric Acid

Hydrofluoric acid was a major impurity in the product from run TU-1. Although the HF content does not present a major difficulty in the conversion of the product to UF_4, it does complicate sampling of the product.

HF and UF_6 exhibit[2,3] a miscibility gap in the temperature range from 61.2 to 101°C for a UF_6 composition range of 9 to 79 formula % UF_6. Therefore, homogeneous samples of the product cannot be obtained at tempera-

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[1] Moncrief, E. C., "Handling of VPP Product by Y-12 Product Processing Department," ORNL-CF-61-6-30, June, 1961.

[2] Rutledge, G. P., R. L. Jarry, and W. Davis, Jr., "Freezing Point Diagram and Liquid-Liquid Solubilities of the System Uranium Hexafluoride-Hydrogen Fluoride," J. Phys. Chem., 57, p. 541 (1953).

[3] Jarry, R. L., F. D. Rosen, C. F. Hale, and W. Davis, Jr., "Liquid-Vapor Equilibrium in the System Uranium Hexafluoride-Hydrogen Fluoride," J. Phys. Chem., 57, p. 909 (1953).

tures below 101°C if the HF content in the UF_6 is sufficient to form compositions in the miscibility gap. For UF_6 - HF compositions in the misicibility gap, homogeneity may be obtained either by sampling at higher temperatures (and increased pressure, i.e., 10 atmospheres at 101°C) or by pumping or "flashing" off the HF and forcing the composition of the mixture toward the homogeneous UF_6 rich region of the phase diagram. The inherent dangers of sampling at 101-105°C under 10 atmospheres pressure eliminated this method of obtaining product homogeneity. Prior to HF removal, sampling procedures would result in only the UF_6 rich phase being sampled.

The removal of the HF from the TU-1 product cylinder was accomplished by "flashing" the HF into the secondary cold trap, FV-220. The product cylinder was placed in a regular ice-water bath at 0°C and allowed to reach equilibrium. The cold trap was cooled to -60°C and evacuated to < 10 mm Hg. The valve between the product cylinder and FV-220 was then opened for 7 minutes to flash the HF. Total TU-1 product cylinder weight loss was 60±10 g, or essentially quantitative removal of the HF. The quantitative HF removal was verified by a vapor pressure measurement of the product at the sampling temperature (72°C).

The removal of HF from the TU-1 product cylinder produced a 8-9 fold increase in the sodium content in the product sample (see Table 1). A small quantity of black-brown particulate material was also collected in the UF_6 sample after HF removal and was determined to be SiO_2 by X-ray diffraction techniques. In addition, a greenish-yellow color was dispersed heterogeneously throughout the sample. The SiO_2 was probably formed by the reaction of SiF_4 (formed by fluorination of Si in the salt and Na_2SiF_6 in NaF) with moisture and HF in the product cylinder, and the SiO_2 being soluble in HF, was not sampled when the miscibility gap existed in the product. The insoluble nature of the SiO_2 on hydrolysis of the UF_6 sample would preclude its presence in the spectrographic analysis presented in section 3.1.2. It is expected that no appreciable carry-over of the SiO_2 will occur on thermal transfer of the UF_6 to the standard cylinder for shipment to Y-12.

3.1.2 Total Cation Impurities

Quantitative spectrographic analysis of the TU-1 product before HF removal indicated a total cation impurity level of < 320 ppm based on UF_6. This level of cation impurity essentially meets A. E. C. product specifi-

cations for return of product (300 ppm total cations based on UF_6). Table 1 summarizes the product impurity before and after HF removal.

Table 1. TU-1 Product Cation Impurities

Element	PPM of UF_6	
	Before HF removal	After HF removal
chromium	2	< 1
copper	31	10
iron	7	2
lithium	< 1	< 2
molybdenum	120	100
sodium	150	1300
nickel	4	3
tin	< 4	2
zirconium	< 1	< 1
Total	< 320	< 1421

The sodium contamination of the product is apparently due to entrainment of sub-micron size NaF fines from the absorbers. The increase in the sodium content of the sample after HF removal can be attributed to solubility in the HF prior to "flashing." The TU-1 product Na contamination after HF removal is a factor of 2-5 above that found in the ARE E-run product.[4]

The molybdenum contamination in the product is due to the formation of volatile MoF_6 during fluorination. The MoF_6 complexes NaF at 100°C much like UF_6 and exhibits a partial pressure of 760 mm at 220°C. Since the INOR-8 dissolver contains 16 wt % Mo, corrosion of the vessel may tend to maintain a high molybdenum contamination of the product. The fact that molybdenum is the end point of several radioactive decay chains may also increase the level in the product during hot runs. Molybdenum was shown to be the major product contaminant during hot cell studies on irradiated Zr-U alloy fuel.[5]

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[4] Whitmarsh, C. L., "Reprocessing of ARE Fuel, Volatility Pilot Plant runs E-3 through E-6," ORNL-CF-59-8-73, August, 1959.

[5] Cathers, G. I., R. L. Jolley, E. C. Moncrief, "Hot Cell Demonstration of the Fused Salt Volatility Process," ORNL-CF-60-3-11, June 3, 1960.

3.2 Isotopic Concentration of Product

Isotopic analyses on samples from the TU-1 product are shown in Table 2.

Table 2. Isotopic Analyses of TU-1 Product*

	Weight %			
Sample No.	U-234	U-235	U-236	U-238
UP-1	0.88	87.52	0.10	11.50
UP-2	0.94	87.95	0.18	10.93
UP-3	0.98	87.84	0.16	11.02
UP-4	0.81	87.33	0.04	11.82
UP-6**	0.86	87.15	0.18	11.81
UP-7**	1.01	86.89	0.21	11.89

* Accuracy ± .25%
** Sampled after "flashing" HF from product cylinder

The fact that the U-235 enrichment was 87% is extremely interesting. Since the fuel for run TU-1 was nonirradiated and fully enriched, the U-235 concentration of the product should have been 93.1%. This would seem to indicate: (1) contamination of the product with depleted uranium during processing, or (2) use of lower enrichment uranium during fuel element fabrication. The possibility of (1) above has been investigated thoroughly and eliminated. The second possibility is being investigated by the SS accountability office.

3.3 Approximate Uranium Balance

As stated in section 3.0, quantitative uranium balances will not be practical over each individual run. The approximate balance shown in Table 3 is indicative of the material collected in the product cylinder, samples, and non-recoverable losses. The "system holdup" figure represents a "by difference" forced balance over the run.

3.4 Fluorinator Sampling

Multiple samples were taken of the molten salt in the fluorinator (FV-100) during run TU-1 as an accountability check against the SS transfer sheets. The weight of salt in the fluorinator was determined by (1) weighing after waste salt transfer, and (2) by calculation from system density and level instruments. Analyses of the salt averaged 3,320 ppm U in the salt. The total uranium charge in the fluorinator by weighing and by calculation respectively, was 645±101 g and 661±103 g. Compared with 530 g in the fuel elements, the SS transfer sheet tally was not within the limit

Table 3. Approximate TU-1 Uranium Balance

Source	Weight U, g	% of Feed
CHARGED:		
Fuel elements	530.	----
Fluorinator feed (by weighing)	645±101	----
Fluorinator feed (by calc.)	661±103	
RECOVERED:		
Product	501.	94.5
NON-RECOVERABLE LOSSES:		
Caustic scrubber (0 mg)	0.	----
Waste salt (223 mg)	0.	----
Caustic neutralizer (69 mg)	0.	----
Off-gas solids (70 mg)	0.	----
Total	0.	0.0
SYSTEM HOLDUP	29.	5.5

*ratio U actual/U theoretical = 0.998

of error of the fluorinator samples by either method of determination. Whether a discrepancy exists or whether sampling and measurement techniques are inaccurate will have to be resolved as additional runs are completed.

4.0 DISSOLUTION STUDIES

Run TU-1 was the first dissolution run in which nonirradiated Zr-U alloy fuel elements were used. However, it was not the first two-element dissolution run (see Results of Volatility Pilot Plant Dissolution Run T-7, ORNL CF-60-12-57). Since the flowsheet demonstration runs (TU- series) are also development runs, operating conditions will be varied systematically throughout the series to achieve optimum operating conditions prior to hot operations.

4.1 Dissolution Run Conditions

Run dates: 2320, 12-30-60 to 2215, 12-31-60

Per cent completion of dissolution, > 95%

Fuel: 2 Zr-U fuel elements (~ 1% U, Zr-2 clad)

Fuel weight, (includes Zr wire) 50.89 Kg

Fused salt charged, 100.8 Kg

Fused salt composition, mole %	
Initial	39.9 - 35.1 - 25.1*
Final (theoretical, for 100% completion)	29.0 - 25.5 - 45.5*
Dissolver lower section temperature,	670 - 490°C
Dissolver vapor section temperature,	562 - 400°C
Run time,	22.9 hr
HF flow rate (avg.),	92 g/min
Submergence of fuel in salt, (initial)	113%

*$NaF-LiF-ZrF_4$

4.2 Dissolution Results

Maximum dissolution rate,	1.46 mg/cm^2 min **
Average dissolution rate for 90% completion,	0.67 mg/cm^2 min**
Average dissolution rate for 90% completion,	2.52 Kg/hr
HF utilization, %	
First 27 minutes,	65.2%
Over-all (maximum),	87.1%
Over-all (average),	35.2%
Off-gas solids collected, g	
in off-gas line,	~ 10-15 g
by cyclone separator,	> 30 g
on porous metal filter,	essentially zero
on copper mesh filter,	250 - 300 g
Final fused salt composition, mole %	
(from analysis)	32.8 - 24.8 - 40.3*

*$NaF-LiF-ZrF_4$

**rates based on total initial area of fuel

4.3 Discussion of Dissolution

4.3.1 Dissolution Rate

The dissolution rate curve for run TU-1 is shown in Fig. 2. The general shape of the curve is typical for dissolutions of plate-type fuel elements. The high peak at 25 to 45 per cent completion probably occurs as a result of the fuel element disintegration.

Dissolution rates expressed in mg/cm^2-min often do not convey a true indication of the dissolution efficiency. For example, a comparison of the average dissolution rate (for 90% completion) for runs T-7 and TU-1 shows 1.06 and 0.67 mg/cm^2-min, respectively, or a ratio of 1.57. However, when

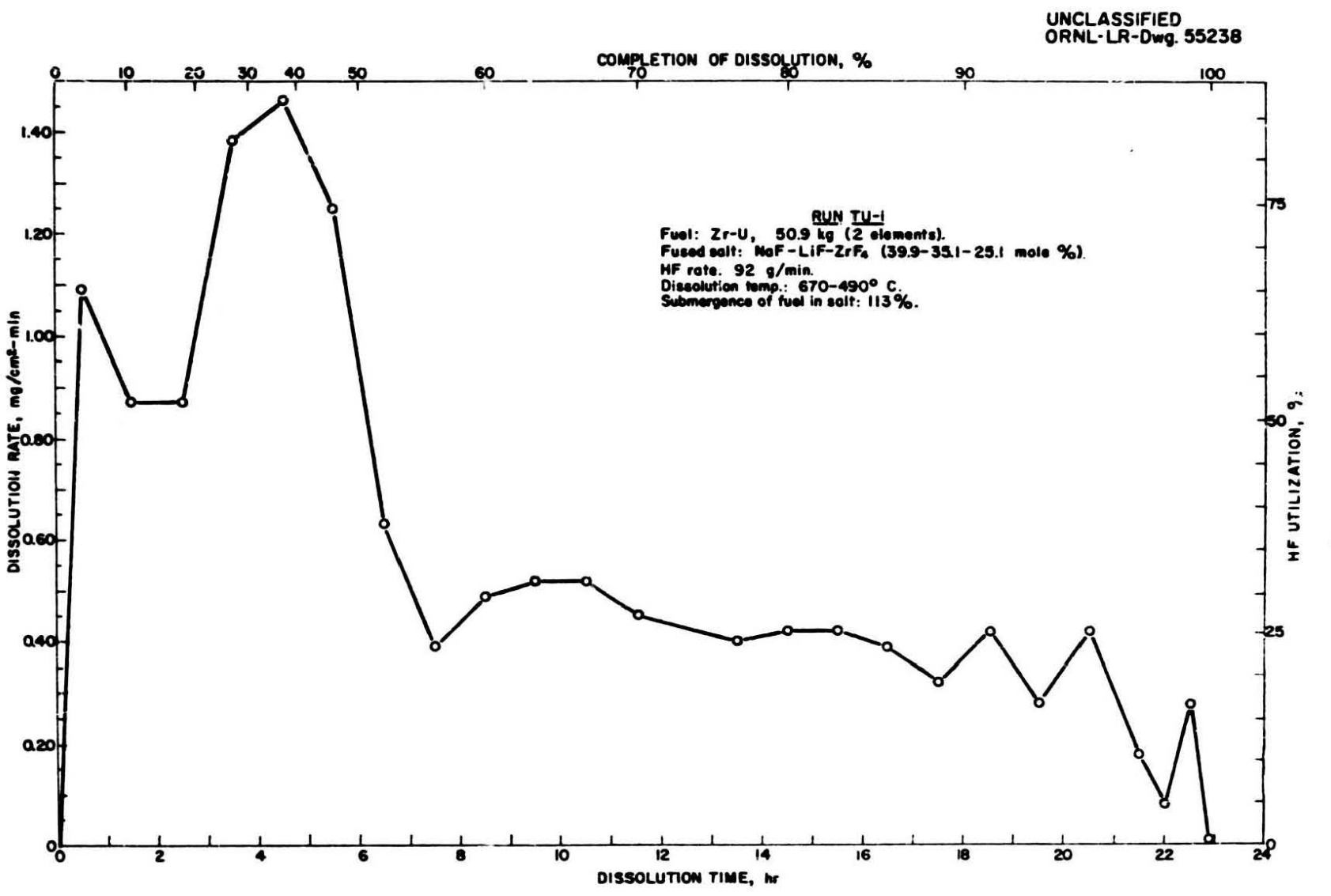

Fig. 2. Dissolution rate and HF utilization during run TU-I.

the rates for the same 90% completion are expressed in Kg/hr exclusive of fuel area, a rate ratio of 1.10 is obtained (2.78 Kg/hr in T-7; 2.52 Kg/hr in TU-1). Thus, variations in the fuel element weight (~ 15% greater in T-7 than in TU-1) and area (~ 43% greater in TU-1 than T-7) during runs can contribute to dissolution rates expressed in mg/cm^2-min which are deceptive. This becomes even more notable where there is doubt as to the true contribution of the internal surface area of the fuel toward the dissolution rate. Therefore, in view of the difficulty in coorelating rates expressed in mg/cm^2-min, future reference to dissolution rates will be in terms of Kg/hr for 90% fuel dissolution.

4.3.2 HF Utilization

Maximum and average HF utilizations in run TU-1 were 87.1 and 35.2%, respectively. The 35.2 figure represents an increase over the average utilization for run T-7 (27.8%). This increase can be attributed to one or more of the following conditions which existed in run TU-1: (1) 43% more fuel element surface area than in run T-7, (2) 18% greater fuel element height than in T-7, and (3) 32% lower HF mass velocity than in T-7. Thus, each of the above factors would contribute to greater HF residence time in proximity to fuel and thereby increase the probability of reaction. It is hoped that future runs under similar geometry conditions will determine the effect of each of the above factors on the HF utilization.

4 3.3 Fused Salt

Nominal initial and final ZrF_4 salt compositions are 25.2 and 45.0 mole %, respectively. The compositions shown in section 4.1 and 4.2 are based on analyses of the salt before and after dissolution of the fuel.

During run TU-1 the salt temperature in the dissolver lower section was maintained approximately 40-60°C above the freezing point of the salt (initial salt, 608°C; final salt, 450°C).

4.3.4 HF Inventory

The HF inventory for run TU-1 is based on an average HF flow rate of 92 g/min.

Total HF charged to system (FV-1006, FV-1207, etc.),	81.3 Kg
Total HF neutralized from system (including dumps from FV-1006, FV-1207, etc., after run),	28.6 Kg
HF used,	52.7 Kg
HF required for dissolution (theoretical),	44.7 Kg
HF unbalance,	8.0 Kg +17.9 %

The large HF unbalance cannot be explained. HF Deviations of this magnitude are not uncommon since runs T-5 and T-6 exceeded ±15.%, and run T-3 +18%. Unfortunately, the fact that run TU-1 was only ~95% completed tends to make the deviation for that run conservative. Although the quantitative value obtained for the HF inventory has deviated greatly in several runs, the use of the liquid level instrument in the HF accumulator (FV-1006) as a measure of the end of dissolution has proved very successful.

4.3.5 Estimate of Dissolver Corrosion

An attempt was made to evaluate the corrosion sustained by FV-1000 during run TU-1. However, since the NaF pellets from the complexible radioactive products (CRP) trap, zone 1 of FV-105, were discharged to the waste salt without sampling, the cation balance for run TU-1 was incomplete. Nevertheless, the cation content for all other streams is presented below for general information.

Table 4. Cation Content in Streams During Run TU-1

	Source	Weight, g			
		Ni	Fe	Cr	Mo
IN:	Feed salt	10	70	26	10
	Fuel element[a]	36	66	82	--
	Total IN	46	136	108	10
OUT:	Waste salt	97	31	31	2
	Off-gas solids[b]	19	83	1	2
	Total OUT	116	114	32	4

[a]Based on analyses of Zr-2: Fe 0.13, Ni 0.07, Cr 0.16 (wt %).

[b]Approximately 345 g collected during Run TU-1.

4.3.6 Off-gas Solids Removal

The generation of sub-micron size solid particles during dissolution continues to complicate the dissolution operation. The mechanism of the solids generation is associated with the reduction of metallic fluoride impurities less active than zirconium (the fuel) and the deposition of these impurities on the fuel at the site of the dissolution reaction.[6] Once

[6]Cathers, G. I., "Thermodynamics in the Fused Salt Dissolution Process for Zirconium Fuel," ORNL-CF-59-11-110, Nov. 19, 1959.

deposited, the metalic impurities (Ni, Fe, etc.) may flake off the fuel element surface, migrate to the surface of the molten salt, and be entrained to the off-gas, or may be oxidized in the presence of HF and molten salt to a soluble form susceptible to re-deposition on other sites of the fuel, thereby creating an oxidation-reduction cycle. Evidence supporting this theory is strengthened by two notable facts: (1) Ni and Fe have been observed to participate in the above oxidation-reduction cycle, and (2) where dissolution conditions are employed without an active material such as zirconium as fuel (copper dummy fuel substituted) the generation of off-gas solids is nil, thereby supporting the theory of generation at the site of an active fuel (zirconium).

Since no satisfactory procedure has been formulated to prevent solids generation (i.e., pretreatment of feed salt to obtain ultra-purity in conjunction with schemes to prevent impurity build-up by dissolver corrosion), the problem becomes one of solids removal rather than suppression of their generation.

A cyclone, backed by a 20 micron sintered inconel filter and a copper scouring pad filter pack, was used in the off-gas line during run TU-1 to prevent plugging of off-gas control valves HCV-1000-1 and HCV-1000-2. In general, the cyclone and backup filters were effective in preventing plugging of the valves although a partial cyclone plug occurred after 18 hours of dissolution when the cyclone vibrator broke loose from the housing. As shown in section 4.2, the majority of the solids passed the cyclone and 20 micron filter and were contained by the scouring pad filter. The appearance of the solids was similar to those collected in the T-series of runs. The electron micrograph shown in Fig. 3 continues to suggest that the larger particles are agglomerates. Table 5 summarizes the analyses of the solids from run TU-1.

With certain exceptions, the analyses of the two samples in Table 5 are similar to those observed for the solids collected on the comparable filter system in run T-7 (see CF-60-12-57, p. 6). The exceptions are the low Ni content of both samples, and the extremely high (27.5%) Fe content of the solids from the scouring pad filter. No explanation can be given for the high Fe value as it is a factor of 2 greater than the maximum Fe content of any solids sample from the entire T-series of runs.

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Fig. 3. Solids from cyclone pot, run TU-1. 20,000 x

Table 5. Analyses of Solids Collected During Run TU-1

Source of Sample	Analyses, wt % (unless indicated otherwise)												
	Na	Li	Zr	Ni	Fe	Cr	F^-	Mo	Sn	Si	Cu	S	U
Cyclone collection pot	5.0	1.5	21.0	3.7	0.3	0.1	48.5	0.7	3.7	< .1	.4	75 PPM	580 PPM
Scouring pad filter	1.9	0.1	1.4	5.6	27.5	0.4	--	0.6	3.4	< .1	--	---	22 PPM

4.3.7 Recycle HF

Recycle HF was sampled after run TU-1 and analyzed 99.8 wt % HF, 0.09 wt % water, and < 0.1 ppm uranium. The water content of the sample was the lowest of any sample to date and may reflect the extra precautions taken during sampling to purge the sample bomb. Individual cation impurities were all < 1 ppm in the liquid HF sample.

5.0 FLUORINATION STUDIES

5.1 Fluorination Conditions

Fluorinator:

Feed: $NaF-LiF-ZrF_4$ - UF_4 salt	
Feed uranium concentration,	3,320 ppm
Fluorination temperature,	500 - 505° C
Fluorine flowrate,	12 SLM
Total fluorine flow time,	150 min

CRP Trap (Zone 1 FV-105):

FV-105 temperature,	400° C
Weight NaF discharged to FV-100 from FV-105 after run, (estimate)	2.0 Kg
FV-105 piston pressure required to discharge,	80 psig
Fixed Bed Absorber, FV-120 temperature,	85 - 120° C

5.2 Fluorination Results

Fluorine utilization (for 99.90% conversion of UF_4 to UF_6),	5.7%
F_2/U (orig) mole ratio (for 99.90% conversion of UF_4 to UF_6)	17.5%
Waste salt uranium concentration, ppm	
After 60 min fluorine sparge	326 ppm
After 90 min fluorine sparge	4 ppm
After 120 min fluorine sparge	4 ppm
After 150 min fluorine sparge	1.2 ppm
Waste salt recovered,	194.5 Kg
Waste salt recovery,	100.5 %

5.3 Discussion of Fluorination

Conversion of the UF_4 in the salt from the dissolver to UF_6 with elemental fluorine was studied in run TU-1. Since both the fluorinator vessel geometry and the salt uranium concentration are markedly different

from fluorinations of the ARE salt, optimum fluorination conditions will be established in the current series of cold uranium runs.

5.3.1 Fluorine Utilization

Table 6 summarizes the results of the 12 SLM fluorination performed in run TU-1. Fluorine utilization was only 5.7% for 99.90% conversion of the UF_4 to UF_6. The corresponding F_2/U mole ratio for this conversion was 17.5 as shown in Table 6. Possible reasons for the high F_2/U mole ratio (F_2/U < 6 normal for ARE processing) in TU-1 are:[7] (1) high impurity level in salt, (2) high fluorine flowrate, and (3) vessel geometry considerations. Initial U concentration in the salt was shown to have only minor significance. Since the average impurity level in the TU-1 feed salt was lower than that in the ARE feed salt, high F_2 flowrate and/or fluorinator geometry factors may account for the high F_2/U mole ratio obtained.

5.3.2 Salt Balance

As shown in section 5.2, the waste salt recovery was 194.5 Kg, or a salt recovery balance of 100.5%. This recovery was approximately the same as the 100.8% average for the T- series of runs.

5.3.3 Waste Salt Composition Deviations

Average deviations of the final salt composition from the theoretical in runs T-1 through T-7 for NaF, LiF, and ZrF_4 were +2.7, +2.2, and -2.2%, respectively. The maximum deviation was +14.1% for NaF in run T-3. The corresponding deviations for run TU-1 were +22.5, -2.2, and -14.5% assuming 100% completion of the dissolution and deducting the 2 Kg of NaF discharged to the waste salt from the movable bed absorber (FV-105). Thus, the NaF and ZrF_4 deviations for run TU-1 were excessive. However, visual examination of the dissolver after the run indicated that undissolved fuel remained in the dissolver, thereby accounting for a portion of the large ZrF_4 deviation. The TU-1 NaF deviation (+22.5%) was the greatest of any run to date. This high deviation might be attributed to a NaF pellet discharge to the waste salt from FV-105 in excess of the 2 Kg estimated of section 5.1. Following fluorination, the contents of the trap was discharged to the waste salt without sampling.

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[7] Cathers, G. I., M. R. Bennett, and R. L. Jolley, "The Fused Salt-Fluoride Volatility Process for Recovering Uranium," ORNL-2661, April 1, 1959.

Table 6. Summary of Run TU-1 Fluorination Results

Fluorine Time, Min.	Uranium Conc. in salt ppm	Wt% of initial U	Uranium Conversion to UF_6, Wt%	Total Fluorine Feed, moles	Uranium in salt, g-moles	F_2/U (original) Mole ratio	Fluorine Utilization, %
0	3,320	100.0	0	0	2.750	---	---
60	326	9.6	90.4	32.2	0.269	11.7	7.7
90	4	0.10	99.90	48.2	0.003	17.5	5.7
120	4	0.10	99.90	64.3	0.003	23.4	4.3
150	1.2	0.03	99.97	80.4	0.001	29.2	3.4

Fluorination Temp: 500-505°C

Fluorine flowrate, 12 SLM

Feed: NaF-LiF-ZrF_4-UF_4 salt

5.3.4 Complexible Radioactive Products (CRP) Trap

Zone 1 of the movable bed absorber functioned as the CRP trap during run TU-1. This trap is necessary during fluorination operations to remove ZrF_4 "snow", entrained salt, and volatile fluorides, i.e., chromium fluoride, from the fluorinator off-gas. In subsequent runs using irradiated fuel certain volatile fission product fluorides will also be retained by the bed.

During run TU-1, the trap prevented plugging of the fluorinator off-gas valves primarily by removing chromium fluoride.

6.0 PRODUCT COLLECTION

6.1 Product Collection Conditions

Absorbers:

Cycle	Absorber Temperatures, °C	
	FV-120	FV-121
Fluorination	85-100	---
Desorption	80-410	85-435

Fluorine flowrate, 1 SLM

Total fluorine flow time, 253 min

Cold Traps:

Product collected in: FV-223

Cold Trap temperatures,	FV-220	-60°C
	FV-222	-48°C

6.2 Product Collection Results (see Section 3.0 for uranium losses)

Weight of uranium recovered as product,	501. g
Per cent recovery of uranium in FV-223,	94.5%

6.3 Discussion of Product Collection

6.3.1 Movable Bed Absorber

Except for zone 1 (CRP trap), the movable bed absorber was not used during run TU-1. However, the fluorinator off-gas flow was routed through FV-105 and to the fixed bed absorbers.

6.3.2 Fixed Bed Absorbers

The sorption-desorption cycle of UF_6 on NaF in the fixed bed absorbers of the VPP has been previously described.[8] In brief, the gaseous products

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[8] Whitmarsh, C. L., and W. H. Carr, "Fused Salt Fuel Processing in the ORNL Volatility Pilot Plant," ORNL-2918, May, 1960.

from the fluorinator are routed through the CRP trap (Zone 1 FV-105) at 400°C and then to the first fixed bed absorber at 100°C where the $UF_6 \cdot 3$ NaF complex is formed. The gas stream is next routed to the chemical trap, FV-124, and finally to the off-gas scrubber tower.

After sorption of the UF_6 is complete, the UF_6 is desorbed from the NaF by simultaneous heating of both fixed bed absorbers to 400°C in an atmosphere of fluorine sweep gas to prevent reduction of the UF_6 to the nonvolatile UF_5. The second absorber, FV-121, serves to decontaminate the UF_6 from fission products during hot operations. The UF_6, after passing through both absorbers is condensed in the product collector, FV-223, held at -60°C.

Operation of the fixed bed absorbers during run TU-1 was satisfactory. Discharge of the beds and subsequent uranium analyses indicated only 0.477 g of uranium retained on the beds after desorption. The 0.477 g uranium was recoverable since the entire contents of the absorbers, minus samples, was charged to the movable bed absorber for run TU-2.

Current plans are to use the movable bed absorber for future runs of the TU-series, but to maintain the fixed bed absorbers operational.

6.3.3 Cold Traps

The two Freon cooled cold traps, FV-220 and FV-222, were used only as backup traps during TU-1 with the small product receiver, FV-223, serving as the primary cold trap.

Cold trap performance during the run was good. As expected, some UF_6 did pass FV-223, but the 95% collected in FV-223 should assure a representative sample of the total desorbed product.