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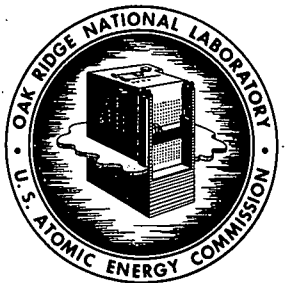
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DATE: May 11, 1959

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SUBJECT: Reprocessing of ARE Fuel, Volatility Pilot Plant Runs E-1 and E-2

TO: F. L. Culler

FROM: C. L. Whitmarsh

ABSTRACT

After two batches ($\sim$ 340 kg) of fluoride salt from the ARE were reprocessed, pilot plant operations were terminated because of a leak through which an estimated 780 g of uranium (as UF_6) escaped. Of the 21 kg of highly enriched uranium in the feed, 93.12% was collected as UF_6 product, 0.13% represented measured losses, and 3.72% was unaccounted for (leak). An additional 3.03% was reclaimed from NaF beds and equipment washes. The product met both chemical purity and activity specifications for product level UF_6. Decontamination from fission products was essentially complete. A gross gamma D. F. was apparently limited by the low activity of the feed salt.

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CONTENTS

1.0 INTRODUCTION

The Fluoride Volatility Process was developed to recover uranium from fused salt reactor fuels. The process consists of volatilization of UF_6 from molten salt by fluorination of the contained UF_4, and additional de-contamination of the UF_6 from volatile or entrained fission product fluorides by sorption and desorption in fixed beds of granular NaF.

A pilot plant scale study was started in December, 1956. Design of the plant was based on a batch process, each batch of salt containing ~ 10 kg of highly enriched uranium. A program of equipment shakedown and process runs with nonradive salt has been completed.

To satisfy a production commitment and to obtain experience with tracer level radioactive salt, a series of "E" runs was performed in which uranium was recovered from the fluoride salt fuel burned in the ARE. Primary emphasis was placed on uranium recovery, with development data being secondary. Although an estimated 6 or 7 runs will be necessary to process the fuel, processing was terminated after the second run due to a leaky system. Processing will be continued after the entire pilot plant is proven gas-tight by a thorough leak test.

2.0 SUMMARY

About 340 kg of fluoride salt containing ~ 21 kg of fully enriched uranium was reprocessed in the Volatility Pilot Plant. This salt had been used to produce 96 Mwhr of nuclear energy (0.006% burnup) in the Aircraft Reactor Experiment and subsequently had cooled for 3 years.

Pilot plant operation was terminated after the second run because of a major uranium loss; UF_6 leaked through a loose flange on a freeze valve vent line. The estimated loss of 780 g of uranium resulted in a plant shutdown until the entire system could be thoroughly leak tested.

Of the material processed, 19.5 kg was recovered as UF_6 product. This material met both chemical purity and activity specifications for product level UF_6. No activity other than that attributed to uranium was detected in the product, thus indicating a gross gamma D. F. for fission products of $> 9 \times 10^4$. This figure was apparently limited only by the low fission product activity in the feed. An additional 637 g of uranium was obtained in a recoverable form--in aqueous solutions and sorbed on NaF pellets--thereby making the gross recovery 96.15% of the feed. The recoverable material was shipped to Y-12 for recovery by aqueous methods.

A major operational problem was plug formation in the CRP trap which necessitated a NaF bed change during fluorination in Run E-2. Subsequent operations involved freezing the salt in the fluorinator and purging with nitrogen to minimize uranium loss and α contamination. Even then the α activity released to the cell air exceeded the maximum permissible concentration (mpc) by a factor of 10^3. At this level filtration is inadequate and masks with a positive air supply are required. Constant air monitors in the cells indicated that most of the α activity (other than that attributed to the UF_6 leak) was released during the following operations:

(1) changing the NaF bed in the CRP trap, (2) molten salt sampling, and (3) product sampling.

3.0 URANIUM MATERIAL BALANCE

The UF_6 product recovered in cylinders (93.12%), plus holdup (0.79%) and NaF beds (2.24%), represented a total recovery of 96.15% of the total uranium in the feed. Measured losses were 0.13% of the feed, and 3.72% was unaccounted for. A leak during Run E-2 released an unknown quantity of UF_6 which apparently escaped through the off-gas system. This loss was estimated to be 768 g by assuming that it represented all unaccounted for uranium.*

The major part (79%) of the uranium trapped on NaF resulted from a plug in the CRP trap, which necessitated the removal of a bed containing ~ 360 g of uranium (as UF_6). The total uranium material balance for Runs E-1 and E-2 is itemized in Table 3.1.

Table 3.1. Total Uranium Material Balance

	E-1	E-2	Post E-2 (both runs)	Total Wt, g	Total % of Feed
Feed	10,585	10,406		20,991	
Product	9,134	10,412		19,546	93.12
Trapped on NaF[a]					
1st Absorber			46		
2nd Absorber			9		
CRP Trap	14	381			
Chemical Trap	7	13			
TOTAL				470	2.24
System Holdup[b]					
F_2 Purge (FV-124)			28		
Wash of H-103-1 Line			123		
Wash of V-106 Line			2		
Wash of Cell I			14		
TOTAL				167	0.79
Losses					
Waste Salt	12	2			
Caustic Solution	3	11			
TOTAL				28	0.13
Accounted for				20,211	
Unaccounted for[c]				780	3.72

a. Recovery was made by dissolution of the NaF pellets and subsequent aqueous processing.

b. Not indicative of total holdup since the entire system was not flushed out.

c. Includes the U which escaped through the off-gas system.

* Subsequent analyses for the material balance indicated 780 g unaccounted for.

Isotopic analyses of the product indicated some depletion of the U-235 enrichment. This represents a loss of 44 g U-235 in addition to that associated with the total uranium loss.

Recovery figures were corroborated by Y-12 measurements on product received.

4.0 PRODUCT PURITY

The UF_6 product from VPP was of sufficient purity to meet product level specifications for material designated for reduction to uranium metal. However, the total cation content exceeded the specifications for UF_6 destined to be returned to a gaseous diffusion cascade (Table 4.1).

Table 4.1. UF_6 Product Purity

Contaminants	ppm, Based on U			
	Run E-1		Run E-2	
	ORNL[a]	Y-12[b]	ORNL[a]	Y-12[b]
Al	-	6	2.5	1.5
B	-	< 0.15	9	< 0.15
Be	-	< 0.015	< 0.05	< 0.15
Ca	-	15	9	15
Cd	-	6	< 10	< 0.3
Co	-	< 1.5	-	< 1.5
Cr	< 30	9	0.7	4.5
Cu	12	45	35	45
Fe	-	22	6.8	22
Hg	< 30	-	-	-
Li	-	< 0.3	-	< 0.3
Mn	-	< 1.5	-	1.5
Mg	-	6	-	< 0.3
Mo	< 30	>150	0.4	30
Na	-	-	< 370	-
Ni	< 34	9	10	111
Si	-	15	1500	< 15
Ti	-	-	260	-
V	-	< 1.5	-	6
Purity, %[c]	100.46	—	99.7	—

a. Spectrographic (Al, B, Be, Ca, Cd, Fe, V), chemical (Cr, Cu, Hg, Mo, Na, Ni, Si, Ti).

b. Spectrographic analysis.

c. Purity = $\dfrac{\text{wt \% uranium}}{\text{Theoretical wt \% uranium}}$.

Of the individual cations investigated, only Cu exceeded specification for both runs. Activity and isotopic analyses were acceptable for product level UF_6 (Tables 4.2 and 4.3).

Table 4.2. Activity of UF_6 Product

Run	Activity, cpm/mg U		
	Gr γ*	Gr β	TRE β
E-1	12	169	< 6
E-2	~ 9	~ 180	< 2
U Background	11	232	-

*Pb absorber.

Table 4.3. Isotopic Concentration of UF_6 Product

Run	Uranium Isotope, wt %				
	234	235	236	238	235/238
E-1	1.19	92.85	0.36	5.60	16.12
E-2	1.16	92.97	0.33	5.54	16.78

Analyses for chemical impurities were conducted on samples taken at ORNL and again at Y-12 prior to reduction to UF_4. Each set of results is listed in Table 4.1. Wide differences were noted in the results from Mo, Ni, and Si analyses.

5.0 DECONTAMINATION FACTORS

Complete decontamination of the UF_6 product from radioactive fission products was attained. No activity other than that attributed to uranium was detected in the product. Thus, the demonstrated fission product gamma D. F. of $> 9 \times 10^4$ was apparently limited only by the activity of the feed. Other D. F.'s, calculated for various stages in the process, are listed in Table 5.1.

Table 5.1. Fission Product D. F. for the Volatility Process

Run	Over-all		Fluorination		CRP Trap		Absorber*
	Gr γ	TRE β	Gr γ	TRE β	Gr γ	TRE β	Gr γ
E-1	$> 8 \times 10^4$	2×10^5	1×10^3	$\sim 10^5$	2.4	~ 2	> 32
E-2	$> 9 \times 10^4$	2×10^5	500	-	5.4	-	> 32

*F. P. activity in absorber assumed to be equally divided between runs.

Fission products which escaped the fluorinator were sorbed on NaF beds (CRP trap, two absorbers, chemical traps) and/or deposited in the

lines. Absence of any fission product activity in the caustic solution used to scrub the off-gas, and on the filter in the off-gas line, indicated that none passed through the system. About 90% of the fission product activity downstream from the fluorinator was due to Cs-137.

In any evaluation of the above data one should consider the low fission product activity ($\sim$ 2 curies per salt batch) present in the feed salt. Accurate analyses necessary for D. F. calculations on specific fission products could not be obtained due to the small amounts present.

6.0 DESCRIPTION OF PROCESS

Fused fluoride salt ($NaF-ZrF_4-UF_4$) contained in the ARE dump tank was melted and drained to a hold tank. Salt batches of $\sim$ 170 kg ($\sim$ 10 kg U) were pressure transferred to the fluorinator for each run. Fluorine was added to the melt in the fluorinator at a rate of $\sim$ 15 slm to oxidize the UF_4 to volatile UF_6. During constant F_2 addition to the melt the fluorination reaction* exhibited three distinct phases: (1) no gas evolution, (2) UF_6 evolution, and (3) F_2 evolution. Although volatilization of UF_6 was $\sim$ 99% complete at the start of phase (3), excess fluorine was added to reduce the final U concentration in the salt to < 25 ppm. Waste salt was pressure transferred to a waste container and taken to a burial ground for radioactive wastes. Volatile fission product fluorides, volatile corrosion product fluorides, and some nonvolatile fluorides (by entrainment) left the fluorinator with the UF_6.
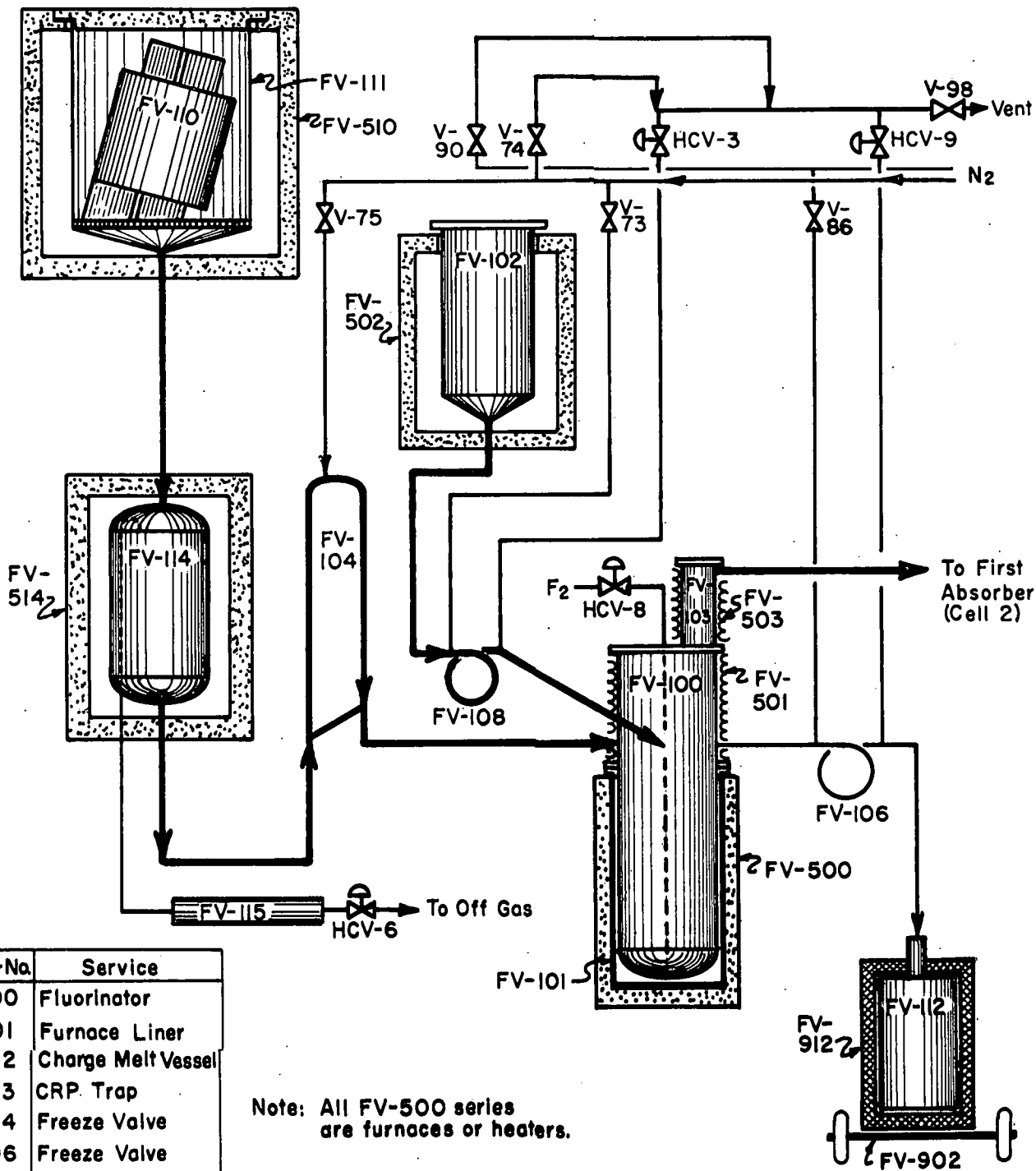
The UF_6 was separated from these other fluorides in the gas stream by sorption** and desorption in fixed beds of NaF pellets. The gas stream from the fluorinator was routed through the CRP trap (at 400°C), both absorbers (at 70°C), a chemical trap (NaF at ambient temperature), and a caustic spray tower. Most of the entrained fluorides and some of the volatile fluorides were sorbed (or filtered) in the CRP trap. The UF_6, plus essentially all the remaining fluorides in the gas stream, was sorbed in the absorbers. The chemical trap served as a safety feature in the event that any UF_6 or radioactive fluorides should reach this point. The remaining gas was scrubbed with 5-10% KOH in a spray tower to neutralize the fluorine and then sent to the off-gas stack. Since the UF_6-NaF sorption reaction*** is forced to the left by increasing temperature, the UF_6 passes through the CRP trap (400°C) and reacts with the absorber bed (70°C). The reaction is exothermic and external cooling (compressed air) is necessary to control the absorber bed temperature.

After the sorption reaction was completed, the UF_6 was desorbed from the NaF, thereby effecting a separation from other sorbed fluorides which have different temperature dependences. Desorption was accomplished by

$$*UF_4 \; (l) + F_2 \; (g) \rightarrow UF_6 \; (g).$$
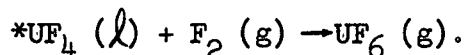
**Uncertainty exists as to the exact type of sorption reaction. However, the reaction vessels are called absorbers.

***$3NaF \; (s) + UF_6 \; (g) \rightleftharpoons UF_6 \cdot 3NaF \; (s)$, ΔH = -23.2 kcal/g mole.

Fig. 6.1

VOLATILITY PILOT PLANT
CELL I FLOWSHEET

FV-No.	Service
100	Fluorinator
101	Furnace Liner
102	Charge Melt Vessel
103	CRP Trap
104	Freeze Valve
106	Freeze Valve
108	Freeze Valve
110	ARE Dump Tank
111	Retort
112	Waste Can
114	ARE Hold Tank
115	Snow Trap

FV-No.	Service
902	Carrier Dolly
912	Shielded Carrier

Note: All FV-500 series
are furnaces or heaters.

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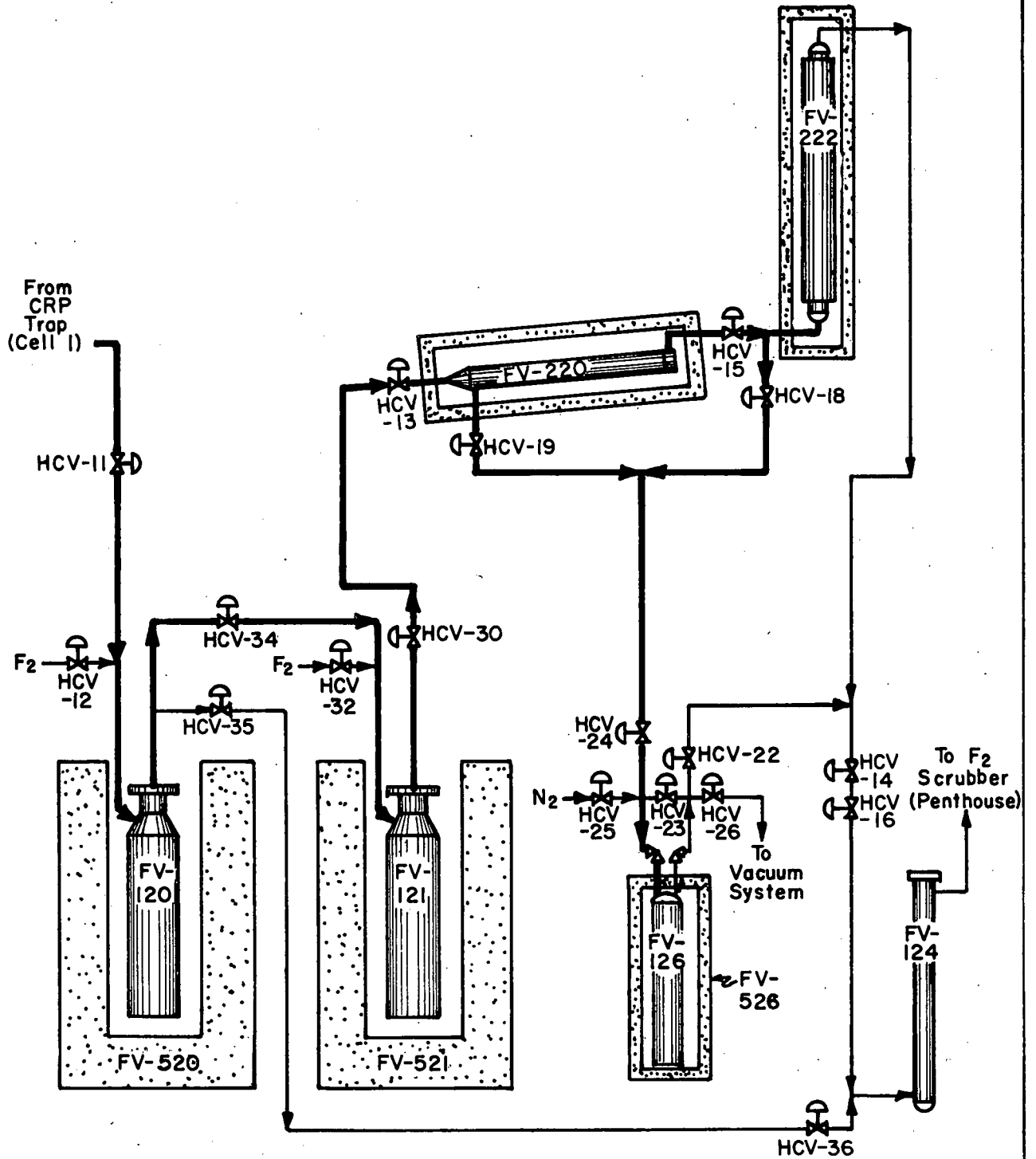
Note: All FV-500 series
are furnaces or heaters

Fig. 6.2

VOLATILITY PILOT PLANT
CELL 2 FLOWSHEET

FV- No.	Service
120	First Absorber
121	Second Absorber
124	Chemical Trap
126	Product Receiver
220	5" Cold Trap
222	6" Cold Trap

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heating both absorber beds simultaneously to 400°C in an atmosphere of fluorine sweep gas (~ 8 slm). The oxidizing atmosphere tends to decrease the rate of formation of nonvolatile UF_5 in the absorbers. After leaving the absorbers the UF_6 was condensed in two cold traps. The bulk of the UF_6 condensed in the first trap, operated at -40°C, and any residual vapors were condensed in the second trap, at -55°C. The off-gas was then routed through a chemical trap and caustic scrubber as in the previous step.

The UF_6 was then liquefied and drained to standard shipping containers by the following procedure. The cold traps and connecting lines were evacuated to < 0.5 mm Hg abs. The system was heated to > 64°C (UF_6 triple point) thereby liquefying the UF_6 in an atmosphere of UF_6 vapor. This liquid was drained to a product receiver. The product receiver was then cooled to 0°C to effect a thermal transfer of UF_6 vapors. After the thermal transfer appeared complete (constant product weight), the cylinder was valved off and the cold traps were cooled to normal operating temperatures. Thus, any UF_6 vapors not transferred were re-condensed in the cold traps and combined with a subsequent run.

The chemistry of the process is described in references 1, 6. Details of pilot plant construction are given in reference 7. The pilot plant flowsheet is shown in Figures 6.1 and 6.2.

7.0 PROCESS MODIFICATIONS

The following flowsheet and equipment modifications were made in order to reprocess the ARE fuel.

A dump tank (FV-111) and a hold tank (FV-114), each enclosed in a furnace (FV-510 and FV-514), were installed to facilitate removal of the salt from the ARE dump tank and to provide a reservoir of molten salt from which batches for individual runs could be withdrawn.

The flow pattern was altered by routing the main gas stream during fluorination through both absorbers in series to provide an additional sorption bed in the event that UF_6 and/or fission product fluorides passed through the first bed.

A bypass line around the CRP trap (FV-103) was installed as an alternate route in the event that the trap plugged during fluorination. Also, a vibrator (installed in Run B-1) was provided to break up any solidification of the FV-103 bed that might occur.

The frequency of changing NaF beds was adjusted to the use of the particular vessel. Past experience indicated that the following schedule would be adequate:

Vessel	Frequency of Bed Renewal	Comments
FV-122	Once per 3 runs	--
FV-124	Once per run	Operations-wise the best time is during product transfer
FV-158	Whenever top layer of pellets is yellow	Trap can be inspected without difficulty
FV-120, -121	None necessary	No limit on the service life of these beds has been determined

8.0 FEED SALT

8.1 History

The fused fluoride salt $(NaF-ZrF_4-UF_4)$ feed to the process had previously been used as nuclear fuel in the Aircraft Reactor Experiment[2] in November, 1954. The uranium was fully enriched and had been subjected to 0.006% burnup (96 Mwhr). In the process of removal from the reactor the fuel was diluted with approximately an equal amount of barren salt used to flush out the reactor.

Table 8.1. Physical Constants*

Nominal Composition: 50 mole % NaF, 47 mole % ZrF_4, 3 mole % UF_4

Density at $600°C$: 3.30 g/cc

Melting Point: $520°C \pm 20°C$

*After barren salt dilution.

8.2 Composition

Chemical, radiochemical, and isotopic analyses were performed on samples of salt taken from the fluorinator prior to fluorination. The results of these analyses are listed in Table 8.2.

Table 8.2. Feed Salt Analysis

A.	Chemical, weight %									
Run	U	Na	Zr	F	Cr	Ni	Fe	Si	Ti	Mo
E-1	5.70	10.49	44.2	42.2	0.056	0.017	0.078	0.080	0.12	0.0015
E-2	5.63	-	38.6	33.6	0.044	0.036	0.033	-	-	-

B.	Radiochemical, cpm/mg U					
	Gr γ	TRE β	Zr γ	Nb γ	Ru γ	Te γ
	9×10^4	2×10^5	2.4×10^2	$< 4 \times 10^2$	$< 2 \times 10^2$	$< 2 \times 10^2$

C.	Isotopic, weight %				
	U-234	U-235	U-236	U-238	235/238
	1.18	93.03	0.35	5.44	17.10

9.0 FLUORINATION

The fluorination step in the pilot plant consisted of transferring the feed salt to the fluorinator, flowing fluorine into the melt (with subsequent volatilization of UF_6), and transferring the waste salt to a waste receiver.

9.1 Plant Operation

The transfer of feed salt from the hold tank to the fluorinator proceeded smoothly in both runs. Transfer was initiated with a pressure of ~ 2 psig and could be controlled reasonably well. The quantity of salt charged to the fluorinator was controlled within ± 2% of the amount desired. The quantity of salt per batch contained ~ 10 kg of uranium each. In addition, sufficient volume (> 39 liters) was required to submerge the draft tube in the fluorinator, and thereby improve mixing in that vessel. Transfer data are itemized in Table 9.1.

Table 9.1. Feed Salt Transfer

Run	Heel from Previous Run, kg	Charge from Hold Tank, kg	Total Feed in Fluorinator		
			Weight, kg	Volume, liters	Uranium, g
E-1	13.3	172.4	185.7	56.3	10,585
E-2	17.4	169.8	187.2	56.7	10,408

Proposed conditions for fluorination in Run E-2 included 20 slm of nitrogen to be added to the fluorine in order to create greater agitation of the salt in the fluorinator. Increased agitation appeared necessary

because of a suspected phase separation in the melt. Salt which adhered to the exterior of sample ladles used for Run E-1 feed salt sampling indicated that a uranium rich phase ($\sim 20\%$ U) might be floating on the surface of the melt (Section 9.4.2). However, additional nitrogen flow was stopped when the system pressure started to increase.

The average fluorine flow rates were less than the specified 20 slm due to (1) misinterpretation of flowmeter readings (installation mixup) and (2) high pressure buildup in the system. Recalibration of the flowmeters after completion of the runs revealed that the high and low pressure connections to the orifice had mistakenly been interchanged. Consequently, all flow rates had to be corrected by a factor equal to the square root of the pressure ratio of the corresponding d. p. cells, e.g., a 20 slm reading represented only 13 slm of F_2. The pressure buildup caused the fluorine rate to eventually be decreased to ~ 4 slm and, on several occasions, to be stopped completely. Pressure increased to ~ 4 psig about one hour after the initial fluorination and remained throughout the fluorination period. Pressure relief measures included changing the NaF bed in FV-103 and the application of additional heat to FV-120.

During fluorination in Run E-2 a leak was discovered through which considerable UF_6 escaped to Cell I atmosphere (Section 9.5). Corrective measures included insertion of a new gasket and tightening a flange on a N_2 vent line to a feed salt freeze valve (FV-108).

The quantity of fluorine used in Run E-1 was insufficient to complete the fluorination reaction. Thus, the waste salt contained 80 ppm uranium. Fluorine flow was stopped prematurely because of a miscalculation of total fluorine. Extrapolation of Fig. 9.1 indicates that a lower uranium concentration could have been attained with additional fluorine.

Waste salt from each run was transferred to the waste salt carrier without difficulty. Some splatter, which increased the radiation hazard, occurred on top of the carrier. Time elapsed from initiation to completion was 10 and 30 min, respectively, for Runs E-1 and E-2. Data for this operation are presented in Table 9.2.

Table 9.2. Process Data for Waste Salt Transfer

Run	Salt Transferred, kg	Heel Left in FV-100, kg	Pressure, psig		Temperature, °C					
			To Initiate Transfer	Max in FV-100	Freeze Valve			Molten Salt Pipes		
					max	min	avg	max	min	avg
E-1	154	17.4	3.8	5.4	600	515	560	740	615	680
E-2	159	15.1	3.8	6.0	600	545	570	670	620	645

9.2 Fluorine Utilization

Fluorine utilization data in Run E-1 were comparable to that obtained from previous experience[3], i. e., ~ 3 mole ratios F_2/U being required to oxidize the UF_4 to UF_6 (Table 9.3). The higher fluorine requirement
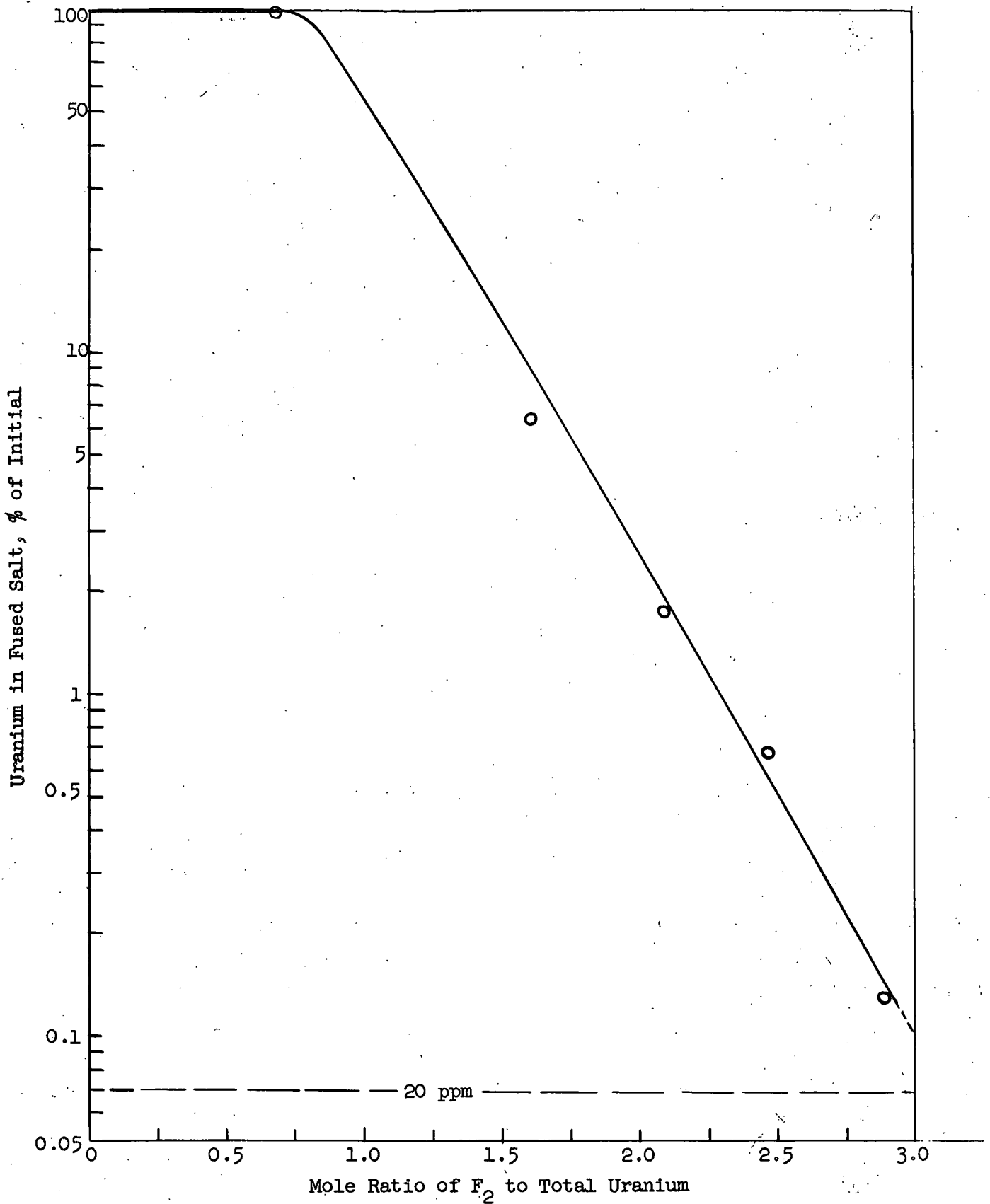
Fig. 9.1. Volatilization of Uranium from Fused Salt in Run E-1

Table 9.3. Fluorine Utilization

| Run | Avg F_2 Flow Rate, slm | Breakthrough | | Total F_2, moles F_2/U* | U Conc. in Waste Salt, ppm | Uranium Volatilized, % of Initial |
		UF_6, moles F_2/U*	F_2, moles F_2/U*			
E-1	13.1	0.66	2.0	2.9	80	99.87
E-2	4.8**	0.86	2.3	5.7	3	99.98

*Moles of initial uranium.

**Prior to pressure buildup (1st hour) flow rate was 12 slm F_2 plus 18 slm N_2.

(5.7 F_2/U) in Run E-2 was indicative of decreased efficiency at low flow rates. A direct comparison is not valid, however, because of additional factors involved, e. g., final uranium concentration, corrosion, possible phase separation, etc.

9.3 Chromium Volatilization

Chromium, present in the feed salt as a corrosion product, was troublesome because of the formation of volatile fluorides--CrF_4 and CrF_5. These compounds had a tendency to settle on valve seats and thereby prevent complete closure. NaF beds have been somewhat effective in removing CrF_5 from the gas stream (Section 9.4.2). Since the fluorination of uranium appears to take precedence over the chromium reaction, ideally one could adjust the fluorine supply such that a minimum of chromium would be volatilized. In practice, however, demarcation between the two reactions is obscure, possibly because of the lack of a quick, reliable method for uranium determination which would indicate the correct time to stop fluorine flow.

The data from Runs E-1 and E-2, presented in Table 9.4, indicate that the rate of CrF_5 volatilization increases substantially as the uranium concentration in the melt decreases.

Table 9.4. CrF_5 Volatilization from Fused Salt

Run	F_2, Total moles	Uranium Conc., ppm	Cr Conc., ppm	% of Initial Cr Volatilized	Avg Rate (Between Samples) of Cr Volatilization, g U/g Cr
E-1	0	57,000	560	0	
	77	3,645	317	43	200
	129	80	35	94	13
E-2	0	56,300	440	0	
	180	273	-	-	158
	255	13	84	81	

9.4 Molten Salt Sampling

The extent of the fluorination reaction was followed by analyses of salt samples taken at various stages of the fluorination. Standard sampling procedure was followed.[4] Sets of 2 to 5 salt samples were obtained simultaneously by lowering the appropriate number of ladles into the molten salt via the fluorinator sample line. These ladles were 3/8-in. copper tubes closed on both ends and notched in the middle. As the ladles were lowered into the melt, they were filled with salt from near the surface, and thus all samples were representative of salt in this region. However, the melt was sparged with nitrogen to attain homogeneity prior to sampling.

9.4.1 Precision

A comparison of uranium analyses between duplicate samples indicated a wider variation than would be expected (Table 9.5). The established

Table 9.5. Molten Salt Samples

Run	Total F_2, mole Ratios F_2/U	Uranium Conc.,* ppm	Variation of U Analysis Between Duplicate Samples, %	Comments
E-1	0	57,000	-	
	1.6	3,645	± 12	
	2.1	1,072	± 57	
	2.5	415	± 42	
	2.9	80	± 16	
	2.9	247	-	From waste receiver before solidification
E-2	0	56,300	-	
	4.0	273	-	
	5.7	13	± 3.9	
	5.7	221	± 65	From waste receiver before solidification

*Average

precision for the fluorimetric and colorimetric method of uranium analysis is ± 5%. Also, samples from the waste receiver had higher uranium content than samples of the same salt in the fluorinator prior to transfer. Altho the % variation between samples ranged up to 65%, the quantity of uranium involved was small. If the greater analysis were assumed to be correct in each case, the loss in waste salt would be increased by 20-30 grams.

9.4.2 Phase Separation in the Fluorinator

The presence of a green scale, which adhered to the exterior of a sample ladle withdrawn from the fluorinator in Run E-1, indicated the possible existence of a phase separation in the melt. At low uranium concentrations $NaF-ZrF_4$ salts are white. This scale was analyzed chemically and by x-ray diffraction with the following results (Table 9.6). The waste

Table 9.6. Analysis of Scale on Sample Ladle

	Concentration, weight %					X-ray Analysis
	U	Zr	Cr	Ni	Fe	
Scale	20.7	18.9	1.13	0.058	0.10	60% UF_5-ZrF_4 S. S. 40% unidentified
Waste Salt	0.36	-	0.032	-	-	-
Feed	5.77	45.0	0.058	0.016	0.075	-

salt (at the time of scale discovery) and feed salt analyses are listed for comparative purposes. The scale was enriched in uranium and chromium by factors of 60 and 20, respectively.

This scale probably was representative of the top layer of salt because this was first to contact the sample ladles. The higher uranium concentration could have been due to the formation of a complex structure which was resistant to fluorination. However, subsequent waste salt samples failed to substantiate this hypothesis.

9.5 CRP Trap Performance

The CRP trap was designed to remove certain volatile fluorides-- principally ZrF_4 and CrF_5--from the fluorinator exit gas by means of sorption or filtration in a bed of NaF pellets. In addition, a certain amount of decontamination was effected by the NaF bed. However, problems of operation, e. g., agglomeration of the pellets (obstructing gas flow) and uranium holdup, caused the desirability of the present design to become questionable.

9.5.1 Operation

Operation of the vessel continued to be difficult, primarily because of high pressure drops across the bed which developed during periods of fluorine flow. These pressure drops (restriction to gas flow) were caused by agglomeration of the pellets into hard masses and plugging of the gas inlet holes, probably with ZrF_4. Various remedies attempted were (1) a vibrator attached to the vessel, (2) temperature variation from 400 to $600°C$, and (3) N_2 flow through the bed. However, none of these was successful.

Immediately after UF_6 started to volatilize in Run E-2, gas flow through the CRP trap was restricted such that the resulting pressure drop

across the vessel prevented continued operation. After the bed was heated to $600^\circ C$ and vibration had failed to reduce the ΔP, the bed was removed-- the bottom half (gas inlet) had to be broken up with a chisel--and re- placed with fresh pellets. About 1/10 of the holes in the gas inlet (re- tainer cone) were plugged with a white powder.

Temperature of the NaF bed was not known with certainty during Runs E-1 and E-2 because only the wall temperature of the vessel was measured. Thermocouples were attached at three points--bottom, middle, and top-- along the wall. Heating units were adjusted to maintain maximum wall tem- perature at $500^\circ C$. Plug formation in Run E-2 resulted in this temperature being raised to $\sim 550^\circ C$ (Fig. 9.2).

9.5.2 Retention of U, Cr, and Zr

Data obtained from analyses of the NaF beds indicated that (1) ura- nium holdup was excessive when a bed had to be changed during fluorination and (2) chromium removal from the gas stream was only 14-20% effective (Table 9.7). The results cannot be considered typical, however, due to mechanical difficulties which interfered with normal operations. Distri- bution profiles of U, Cr, Si, and Zr caught in the CRP trap are shown in Fig. 9.3.

Table 9.7. Retention of Materials by CRP Trap

		U		Cr		Zr	Si	Ti
	Run	Wt, g	% of Total	Wt, g	% of Total	Wt, g	Wt, g	Wt, g
E-1		14	0.1	13.4	14	6.7	18	-
E-2	1st Bed*	369	3.5	4.3	6	12.4	24	1.7
	2nd Bed	12	0.1	9.7	14	14.0	16	2.7

*Removed when bed plugged during fluorination.

In each case chromium tended to remain near the bed inlet (bottom), thus indicating a sorption reaction between CrF_5 and NaF. Uranium concen- tration decreased significantly near the center of the bed, possibly due to the higher temperature in this region. Zirconium distribution, repre- sented by a fairly uniform concentration decrease across the bed, indi- cated removal by a filtration mechanism. Silicon, which was investigated because of the formation of volatile SiF_4, showed a concentration profile similar to that of uranium. The data, however, were somewhat inconclusive due to the presence of Na_2SiF_6 in the NaF pellets. Titanium data were erratic.

9.5.3 Retention of Fission Products

The CRP trap, although primarily intended to be a trap for chemical contamination, also removed certain fission products from the gas leaving the fluorinator. Radiochemical data indicated that $\sim 75\%$ of Gr γ activity

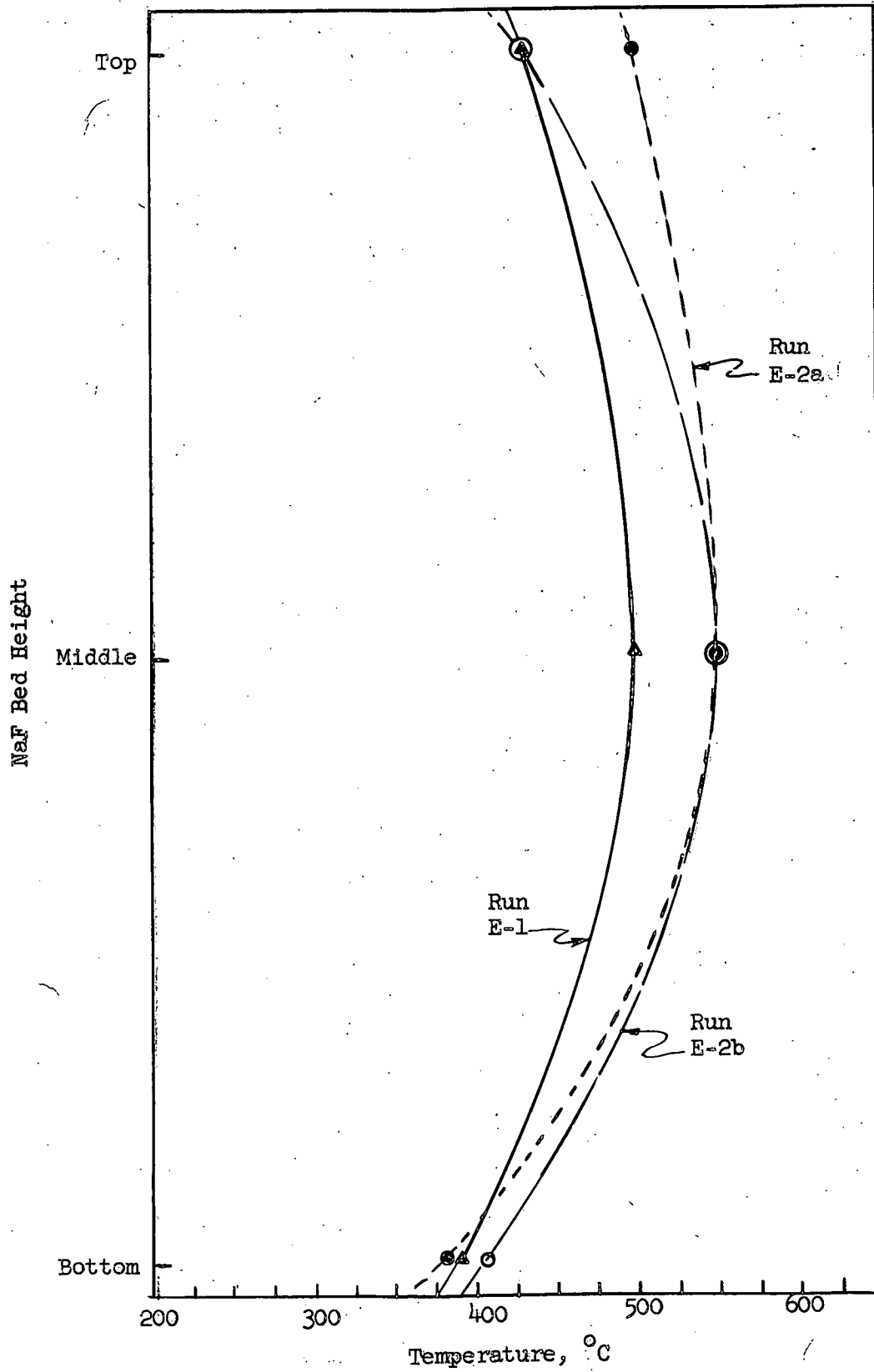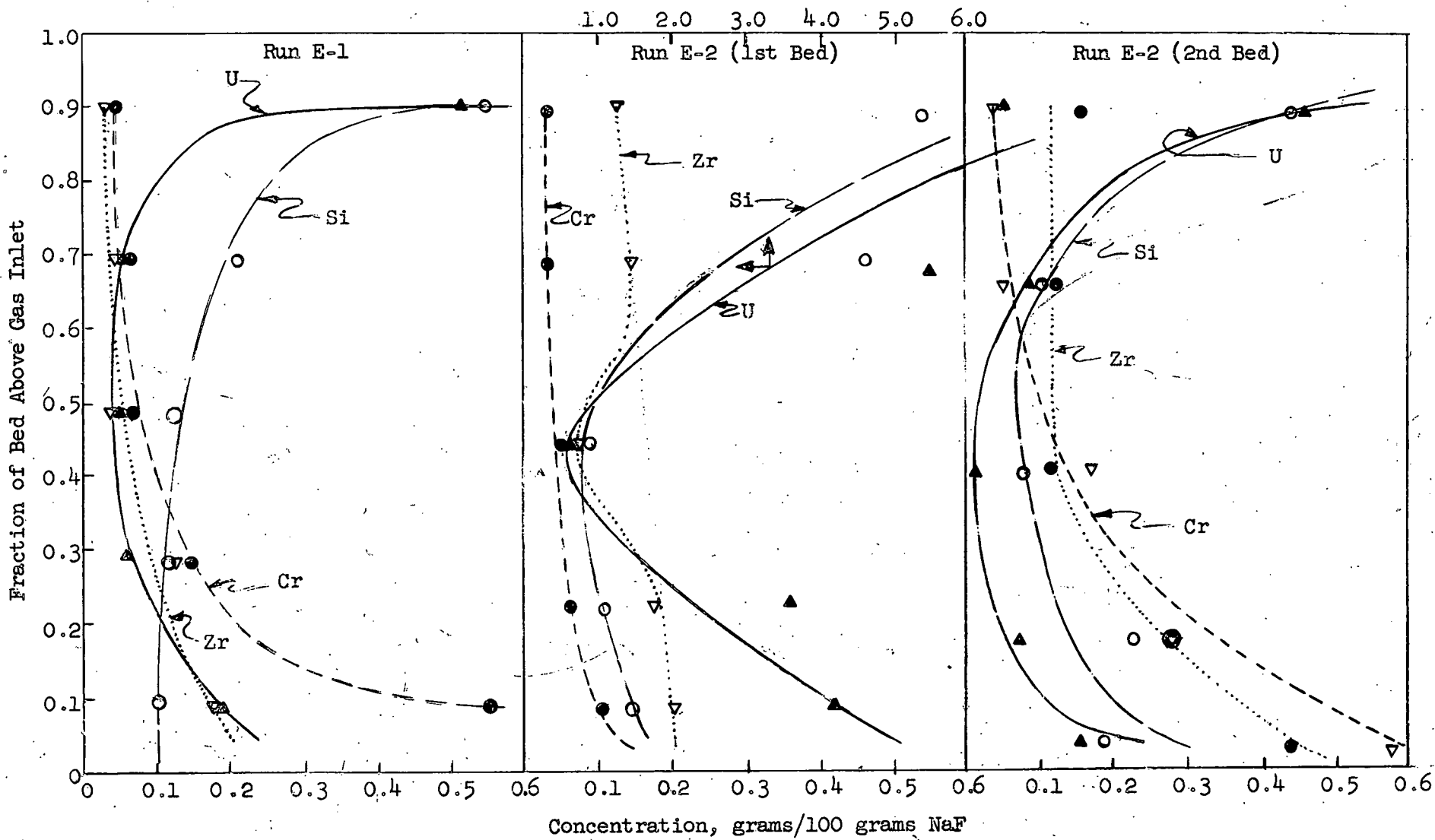Fig. 9.2. Temperature Distribution in CRP Trap

Fig. 9.3. Distribution of Retained Fluorides in the CRP Trap

which escaped the fluorinator was caught in the CRP trap. Most of the β-γ activity on the bed was due to Cs-137, which apparently was entrained in the gas stream (b. p. CsF = 1250°C).

Data from the individual runs are listed in Table 9.8 and the distri-

Table 9.8. Radioactivity on the CRP Trap Bed

Run		Gr β cpm/mg U	Gr γ cpm/mg U	Nb γ cpm/mg U	TRE β cpm/mg U
E-1		13	46	9.4	1.7
E-2	1st Bed	-	52	6.8	1.1
	2nd Bed	-	93	14	1.1

bution of radioactivity is shown in Fig. 9.4. Nb γ activity was concentrated at the gas inlet to the bed whereas the Gr γ appeared to be inversely related to bed temperature.

9.6 UF$_6$ Leak

Near the end of the fluorination procedure in Run E-2 a leak (observed as white smoke) was discovered through which UF$_6$ was escaping from the process to Cell I. The leak occurred at a loose flange located on a nitrogen purge line to a freeze valve on the upstream side of the fluorinator (Fig. 9.5). Ordinarily a positive nitrogen pressure of 4 psig was maintained in the line, but the leak caused UF$_6$ to back up from the fluorinator. After the fluorine had been cut off, a new gasket was installed and the flange was tightened. Close observation revealed no subsequent leakage of UF$_6$ from this region.

Discovery occurred after 3.3 mole ratios of F$_2$/U had been added to the melt, but the duration of the leak was unknown. Its magnitude was estimated to be 780 g uranium, the quantity unaccounted for in the material balance. Analysis of the filter from the off-gas stack indicated that ~ 14 g U passed through the stack during the period in question. Also, an undetermined quantity of UF$_6$ condensed on any cool surface available in Cell I. Part of this was recovered during the cell clean-up after Run E-2, and the remainder was undetected.

10.0 SORPTION OF UF$_6$

The UF$_6$ in the gas stream from the CRP trap underwent additional decontamination from volatile fission product fluorides by sorption-desorption* on fixed beds of 1/8-in. NaF pellets. Two absorbers, each containing ~ 27 kg of NaF pellets and ~ 18 kg of nickel shot, were arranged in series. The nickel shot was placed around the gas inlet to provide a dispersion medium for the gas before it entered the absorption bed.
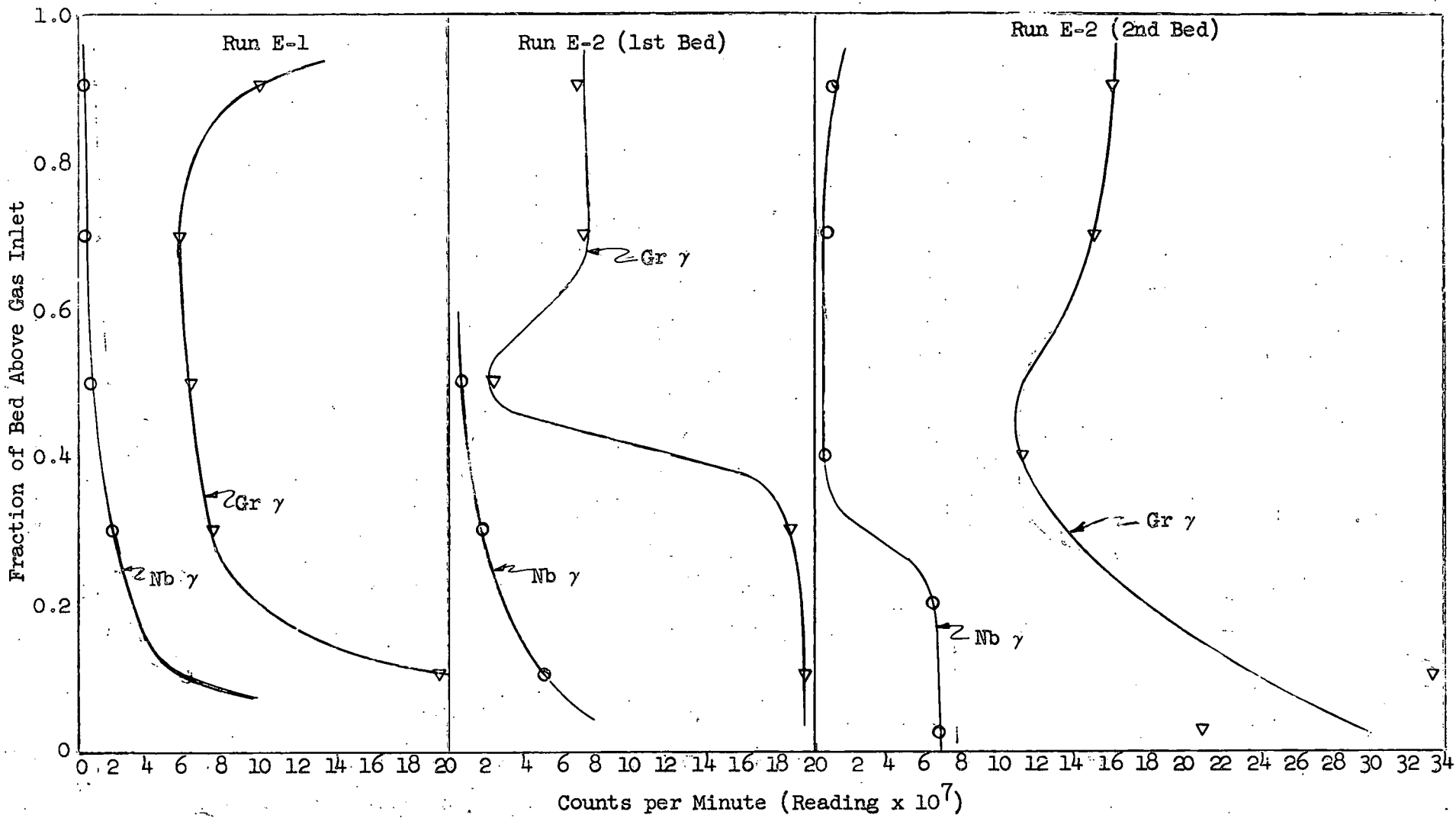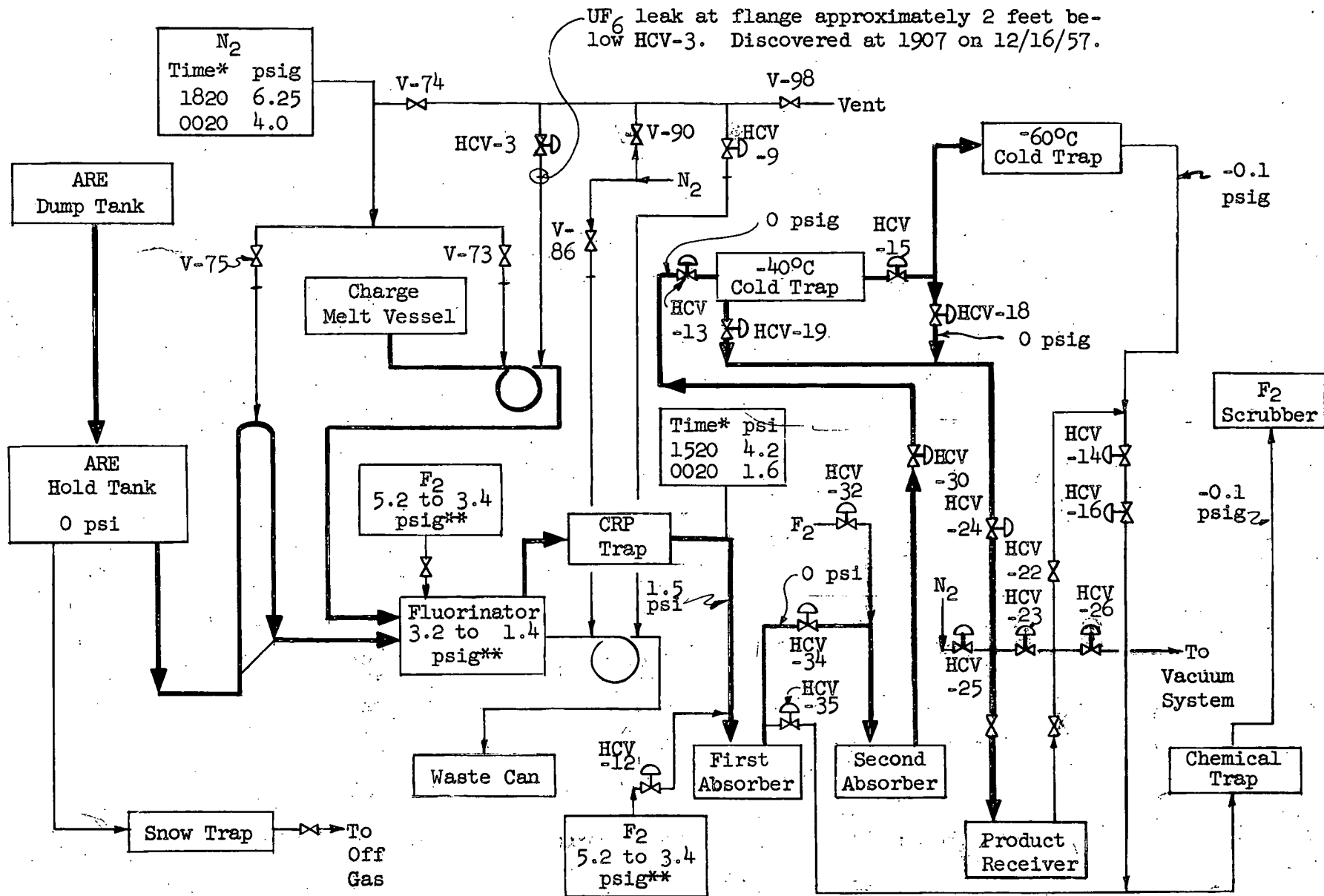
$$*3NaF + UF_6 \underset{300-400°C}{\overset{100°C}{\rightleftharpoons}} UF_6 \cdot 3NaF, \quad \Delta H = 23.2 \text{ kcal/g mole}.$$
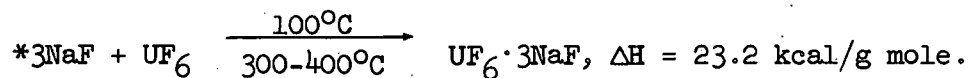
Fig. 9.4. Distribution of Fission Product Activity in the CRP Trap

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Fig. 9.5. Pressures Measured in VPP at the Time of the UF_6 Leak

10.1 Plant Operation

From an operations standpoint, sorption is considered an integral part of the fluorination operation. Consequently, any difficulties are generally included in Section 9.1.

10.2 Absorber Performance

10.2.1 Uranium Loss

No direct measurement was made of uranium losses during the absorption operation. However, one can conclude from the total uranium (20 g) trapped in the chemical trap (FV-124) during Runs E-1 and E-2 that the loss was < 0.10% of the feed. However, this absorption loss (UF_6 that passed through the absorber beds without being sorbed) is not an actual process loss because the uranium can be recovered from NaF.

10.2.2 Bed Temperatures

Control of the NaF bed temperatures was necessary to prevent (a) excessive UF_6 losses to the exit gas and (b) deposition of solid UF_6 at the absorber gas inlet. Temperatures of various parts of each absorber bed during the sorption of UF_6 are shown in Figs. 15.2 and 15.3. The exothermic sorption reaction can easily be followed on the curves in the absence of any change in external heating. Compressed air, circulated in the annular space between the absorber and its furnace, was used to decrease the temperature rise resulting from the heat of reaction.

A maximum bed temperature of $220^{\circ}C$ and $140^{\circ}C$ was reached in Runs E-1 and E-2, respectively. This peak was dependent on operation of the cooling air and the rate of UF_6 flow to the absorber. A temperature rise of $50^{\circ}C$ in the second absorber bed indicated that UF_6 broke through the first bed in Run E-2. Since the uranium feed was not sufficient to exceed the capacity of the NaF, the gas probably channeled through the bed.

11.0 DESORPTION OF UF_6

UF_6 was desorbed from the NaF beds to recover the uranium and to provide additional decontamination from those fission products fluorides which also sorbed on NaF. Desorption was accomplished by heating the beds to a temperature of ~ $400^{\circ}C$ in an atmosphere of fluorine sweep gas. The desorbed UF_6 was then routed through two cold traps in series, where it condensed as a solid. These traps were maintained at $-40^{\circ}C$ and $-52^{\circ}C$, respectively.

11.1 Plant Operation

No operational difficulties were encountered during the desorption and cold trapping of UF_6. After Run E-2 the absorbers were disassembled, and the NaF beds were sampled in sections.[5] Process data recorded during the runs are listed in Table 11.1.

Table 11.1.   Process Data for Desorption and Cold Trapping

Run	F_2 Flow Rate, slm	Temperature, °C				First Cold Trap	Second Cold Trap	Scrubber Solution
		First Absorber		Second Absorber				
		Wall	Bed	Wall	Bed			
E-1	8.2	120-425	100-400	105-445	100-410	-42	-54	20 - 33
E-2	6.5	95-425	90-400	85-425	80-400	-40	-53	24 - 40

11.2 Absorber Performance

11.2.1 Bed Temperatures

Temperatures of the vessel wall, furnace, and the axial center of the bed at three levels were recorded during the runs. These data are included in the Appendix as Fig. 15.4 through 15.7. The curves are typical of those encountered in previous runs,[1] showing (1) a plateau during the period when the rate of UF_6 desorption was greatest and (2) a period of 9-9.5 hr required for complete desorption. In Run E-2 the lower rate of temperature increase in the bottom of the bed (2nd absorber) indicated UF_6 in that region.

11.2.2 Retention of U and Cr

The distribution of U and Cr in the NaF beds of the two absorbers is shown by Fig. 11.1, and the data are summarized in Table 11.2. In general,

Table 11.2. Retention of Materials on Absorber Beds

Absorber	Uranium, g	Chromium, g	Others
FV-120	45.9	36.5	Spot checks made for Si and Ti indi-
FV-121	8.8	16.7	cated no significant quantities present

the materials sorbed at the gas inlet. However, U exhibited a reverse behavior in the first absorber where the top one-eighth of the bed contained two-thirds of the total uranium.

11.2.3 Retention of Fission Products

The first absorber effectively removed fission product activity from the gas stream. About one-half of the gross β-γ activity present in bed was retained in the first one-eighth of the NaF pellets (gas inlet). No significant quantity of activity was detected in the second absorber bed.

The distribution of activity throughout the first absorber bed is shown in Fig. 11.2. Several samples in the bottom and in the top of the bed were analyzed, and the results were extrapolated.
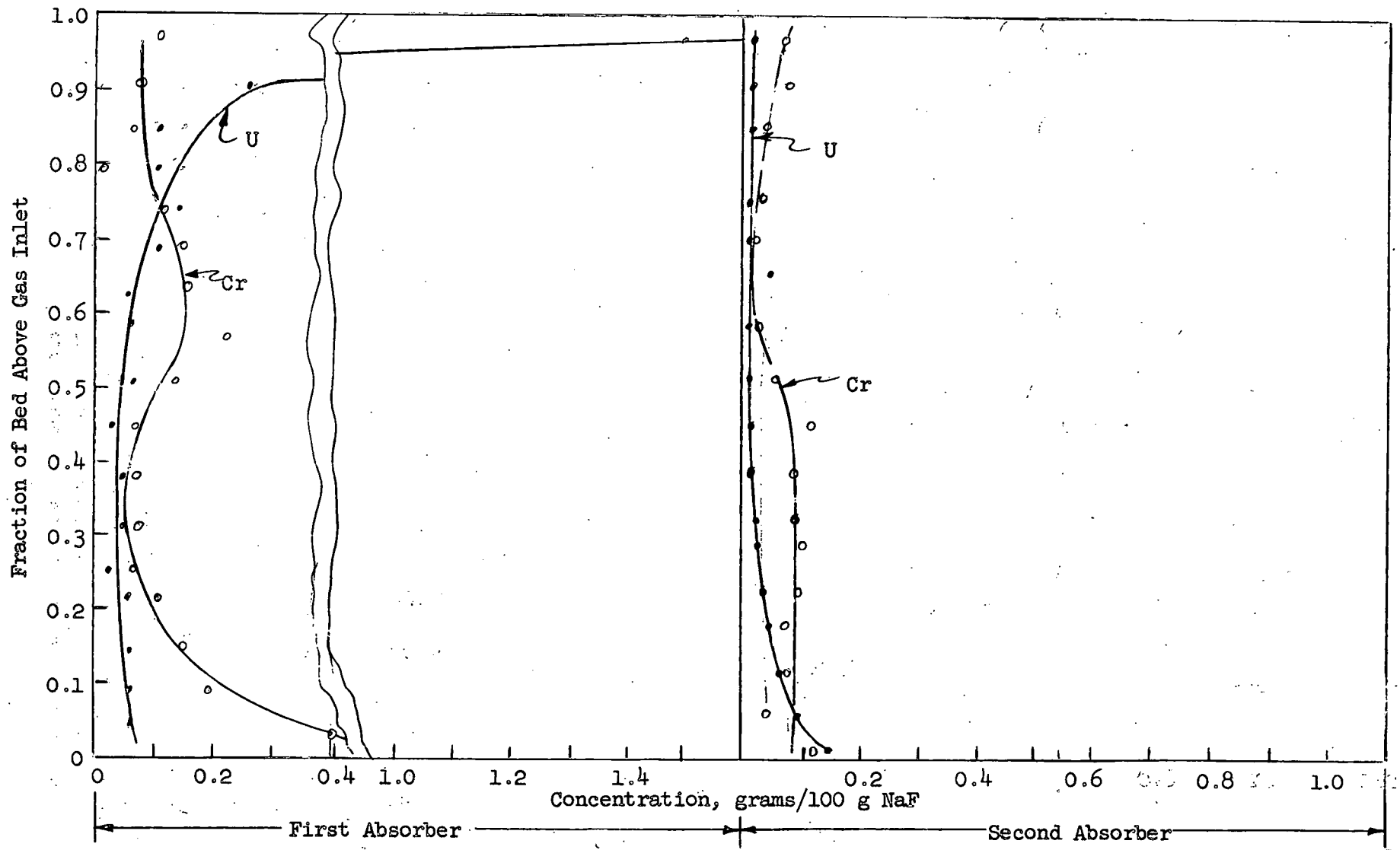
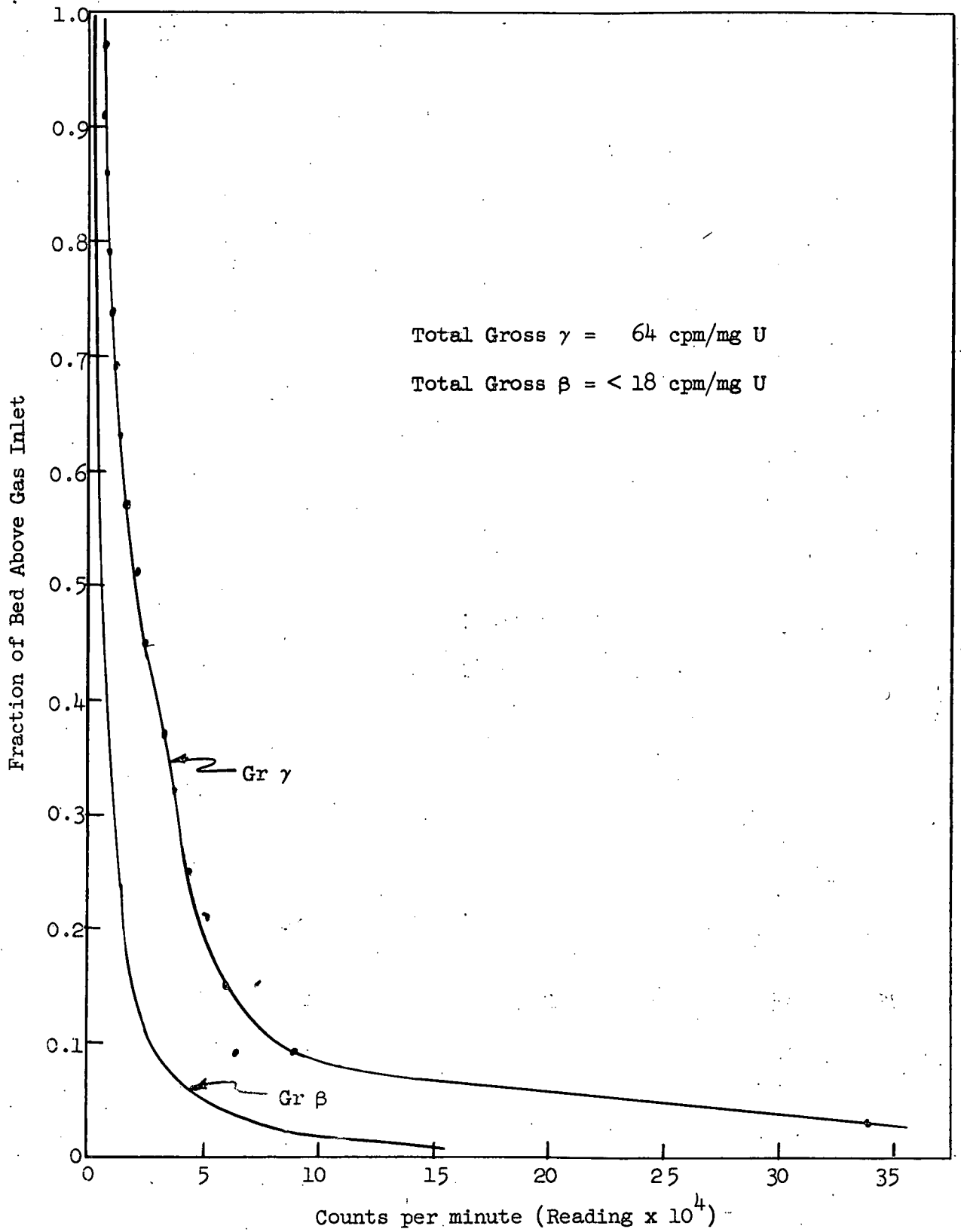Fig. 11.1. Distribution of Uranium and Chromium in the Absorbers

Fig. 11.2. Distribution of Fission Product Activity in the First Absorber

11.2.4 Physical Condition of Absorbers

Inspection of the interior walls of the two absorber vessels re-vealed a thin scale which extended from top to bottom and flaked off easily. Similar scale formation had been noted in previous runs.[3] Also, the gas inlet to FV-120 was almost completely plugged.

The NaF bed contained colored pellets dispersed in an annular ring adjacent to the vessel wall with white pellets in the center. The colored pellets varied from brown to green to yellow and the quantity decreased from bottom to top of the bed. Activity of the bottom third of the first absorber bed was 75 mr/hr at contact (NaF pellets) as measured with a "cutie pie." The remainder of the first bed and the second were < 20 mr/hr at contact.

12.0 PRODUCT TRANSFER

Solid UF_6 in the cold traps was liquefied with heat and pressure.* After the liquid was drained to the product receiver, residual vapors were recovered by thermal transfer.

12.1 Plant Operation

The transfer of UF_6 product from the cold traps to the product cyl-inder was performed without mishap. At the end of the procedure in Run E-1 the weight increase of the product cylinder was only 10 kg instead of the expected 15 kg. A repeat of the product transfer operation recovered an additional 1.6 kg. In Run E-2 the weight of the cylinder started to increase prior to the time the drain valves were opened, thus indicating solid UF_6 had been left in the line from the previous run and/or leakage of the drain valves.

Sampling of the product cylinders was not satisfactory. The sampling manifold became plugged on several occasions, and UF_6 escaped to the cell atmosphere. Although the loss of uranium was insignificant, the air-borne α activity created a biological hazard.

Pertinent data recorded during the product transfer operation are presented in the Appendix in Fig. 15.8 through 15.10.

12.2 Recovery

Product from each run was collected in a standard shipping cylinder (25 kg UF_6 capacity), weighed, and sampled. The samples were analyzed by chemical, radiochemical, spectrographic, and isotopic methods (Section 4.0).

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*UF_6 triple point at $64^{\circ}C$ and 22.4 psia.

Table 12.1. Product Recovery

Run	UF$_6$, g	U Analysis, g/g	Uranium, g	% of Feed
E-1	13,500	0.6766	9,134	86.29
E-2	15,465	0.6733	10,413	100.1
Total	28,965		19,547	

12.3 Chemical Traps

Three chemical traps, fixed beds of NaF pellets, were in the system primarily to sorb uranium from off-gas streams. This uranium is not considered a process loss because it can be recovered by aqueous dissolution of the NaF, followed by aqueous processing.

The main chemical trap (FV-124) was scheduled to be recharged with NaF once per run. From the standpoint of ease of operation the most advantageous time to do this was during the product transfer operation. The other two traps (FV-122 and FV-158) were inspected once per run, but were not changed because of the absence of any yellow pellets (considered indicative of sorbed UF$_6$).

In Table 12.2 the data from analyses of these beds are summarized.

Table 12.2. Analysis of Chemical Trap Beds

Vessels	When Sampled	U, g	Cr, g
FV-124	After Desorption, E-1	7.2	1.0
FV-124	After Desorption, E-2	12.9	1.4

13.0 PERSONNEL EXPOSURE

Biological hazards to personnel were, in order of importance: (1) α radiation from uranium and (2) β-γ radiation from fission products in the feed salt.

Alpha contamination of the cell atmosphere reached a maximum of 2×10^{-8} μc/cc of air (mpc without masks = 5×10^{-11} μc/cc of air) shortly after the bed in the CRP trap had been changed during Run E-2. Other excessively high activities were observed during salt sampling and at the time of the UF$_6$ leak.

The greatest β-γ radiation levels existed around the fluorinator and the waste salt carrier. Measurements made in these areas with a "cutie pie" survey meter ranged up to 700 mr/hr at contact, with the waste carrier lid removed. Working time around the fluorinator was ~ 18 min due to the dose rate of 200 mr/hr in that area. No β-γ radiation could be detected in Cell II—absorbers, product cylinder, etc. Measurements were made against the exterior wall of these vessels.

Results from film badges for the last quarter of 1957 showed no over-exposures among VPP personnel. Specific exposures are not reported because VPP operators worked in the Thorex Pilot Plant for a considerable part of this period, and it is not possible to differentiate between the two as to the source of exposure.

14.0 REFERENCES

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3. C. L. Whitmarsh, "A Series of Seven Flowsheet Studies with Nonradive Salt, Volatility Pilot Plant Runs C-9 through C-15," CF-58-5-113, May 12, 1958.

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5. C. L. Whitmarsh, "Volatility Pilot Plant Run C-3," CF-57-8-95, August 15, 1957.

6. G. I. Cathers, "Uranium Recovery for Spent Fuel by Dissolution in fused Salt and Fluorination," Nuclear Science and Engineering, Vol. 2, No. 6, November 1957.

7. R. P. Milford, "Engineering Design of Oak Ridge Fluoride Volatility Pilot Plant," Industrial and Engineering Chemistry, Vol. 50, No. 2, February 1958.

15.0 APPENDIX

15.1 Run Schedule

Run Schedule					
Run Number	Date Started	Time Started	Date Ended	Time Ended	Total Time, hours
Salt Transfer FV-110 to FV-114	12- 5-57	1005	12- 5-57	1605	6
E-1	12-12-57	0533	12-14-57	1000	50.5
E-2	12-14-57	1035	12-19-57	1500	124.5

15.2 Salt Removal from ARE Dump Tank

The dump tank from the Aircraft Reactor Experiment contained the fused salt nuclear fuel plus barren salt used to flush out the reactor after shutdown. This tank was lowered into a melt vessel (FV-111) enclosed in a furnace. The salt was then melted and drained to a hold tank (FV-114) from which it could be withdrawn in batches for processing.

Measurement of the total salt drained to FV-114 indicated a deficit of ~ 150 kg from the expected amount.

Weight of Salt, kg				
Dynalog Gauge		Process Instrument		Calculated
Gross	1980	Final	982	
Tare	1030	Initial	0	
Net	950	Net	982	~ 1100

Inspection of the dump tank furnace liner revealed that no salt remained in that vessel (Fig. 15.1). Also, radiation measurements plus
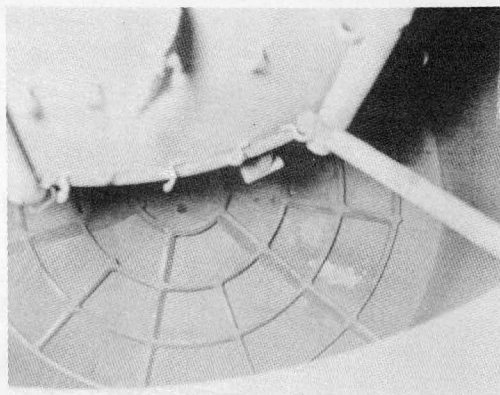
Fig. 15.1. Dump Tank Furnace Liner After Salt was Melted from the ARE Dump Tank and Drained to VPP Hold Tank

visual inspection indicated that no significant quantity of salt remained in the ARE dump tank. Therefore, one can only assume that the entire fuel charge did not drain from the reactor.

15.3 Equipment Clean-out

Due to the major UF_6 leak and the resulting uncertainty of uranium accountability, all accessible areas were washed with water, and the system was purged with fluorine to recover all available uranium. Fluorine was flowed through the system from the fluorinator to the caustic scrubber column at a rate of 2.9 slm for 87 hr. Any UF_6 in the gas stream was trapped by the NaF bed in FV-124. Additional recovery operations included water flushing the main process line (H-103-1) from the CRP trap to the valve. The uranium recovery figures are tabulated below.

Table 15.2. Uranium Recovery from Cleanup Operations

Operation	Weight of U, g	Remarks
F_2 purge	28	Collected on NaF in FV-124
H_2O wash of H-103-1 line	123	Dilute aq. sol'n. ($\sim$ 0.2 g/l)
H_2O wash of V-106-1 line	2	Dilute aq. sol'n. ($\sim$ 0.02 g/l)
Wash of cell walls, floor, and external equipment surfaces	14	Dilute aq. sol'n. ($\sim$ 9 g/l)
TOTAL	167	

15.4 Uranium Recovery from NaF Dissolutions by Ion Exchange

An ion exchange column was designed to recover uranium from NaF bed dissolutions. However, due to restrictions of time and facilities, the column was never developed to the point of successful operation.

The solutions for recovery resulted from dissolution of the absorber and chemical trap beds and were of the general form--2% NaF, 0.001 to 1% U, enough HF to maintain a pH of 1, and the remainder H_2O. The column consisted of a 4-in. dia, 4-ft PVC pipe packed with Dowex-1 anion exchange resin. Because of the corrosive nature of the solutions, all auxiliary equipment was constructed or lined with PVC or Saran.

Proposed operation was to load the column with UO_2^{++} from the feed solution and then elute with HNO_3, the final form of the uranium being UNH. Development studies included feed adjustment, flow rate, residence time, and flow direction. Primarily because of a preferential reaction between Na^+ and the resin, the raffinate concentration was never reduced to < 0.001% U, the design criterion for economic operation. However, with additional development work ion exchange still represents a possible method of uranium recovery from NaF bed dissolutions.

15.5 Process Data

The following data were obtained from strip chart recorders operated during the runs:
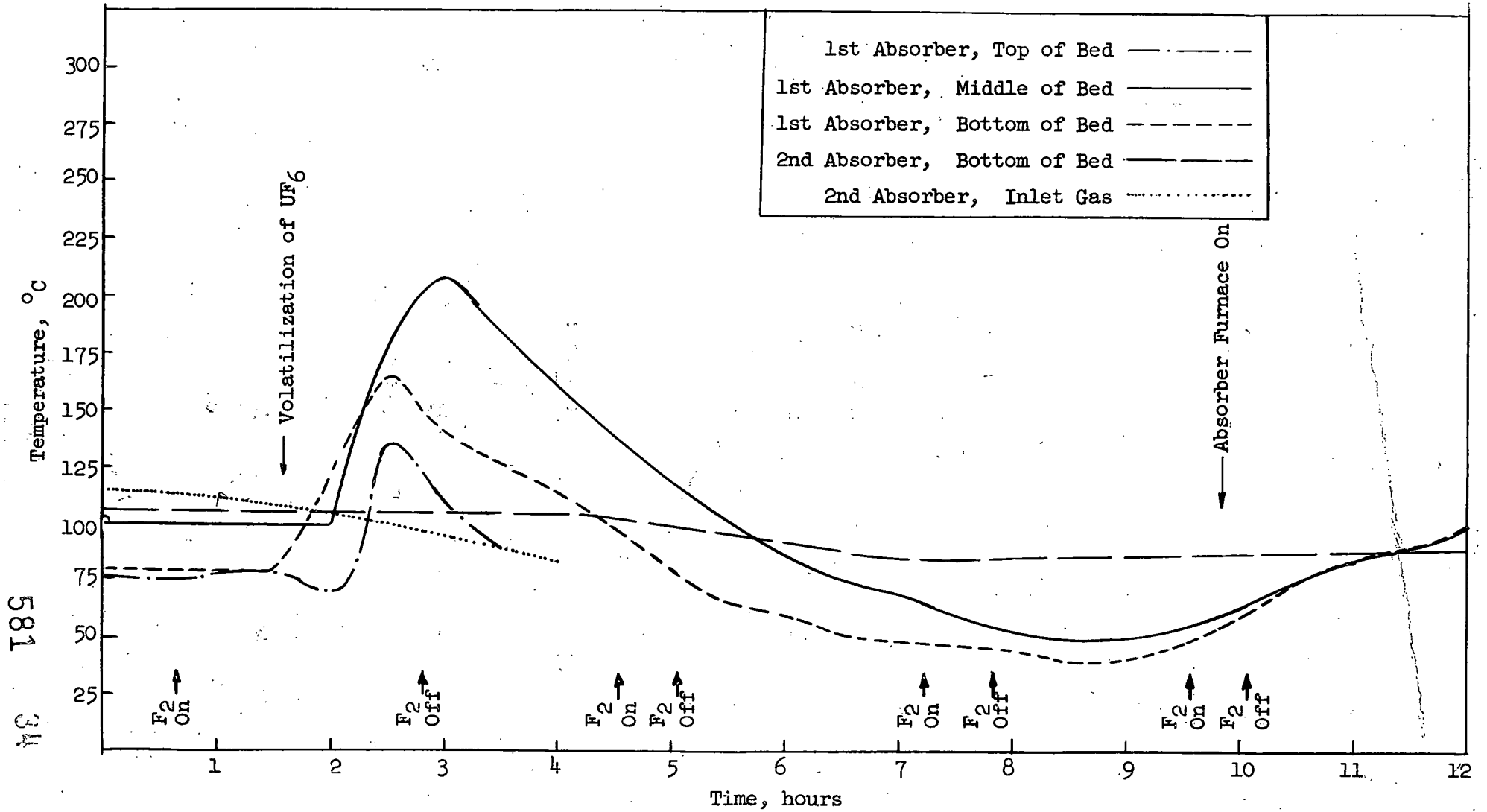
CLW:lj

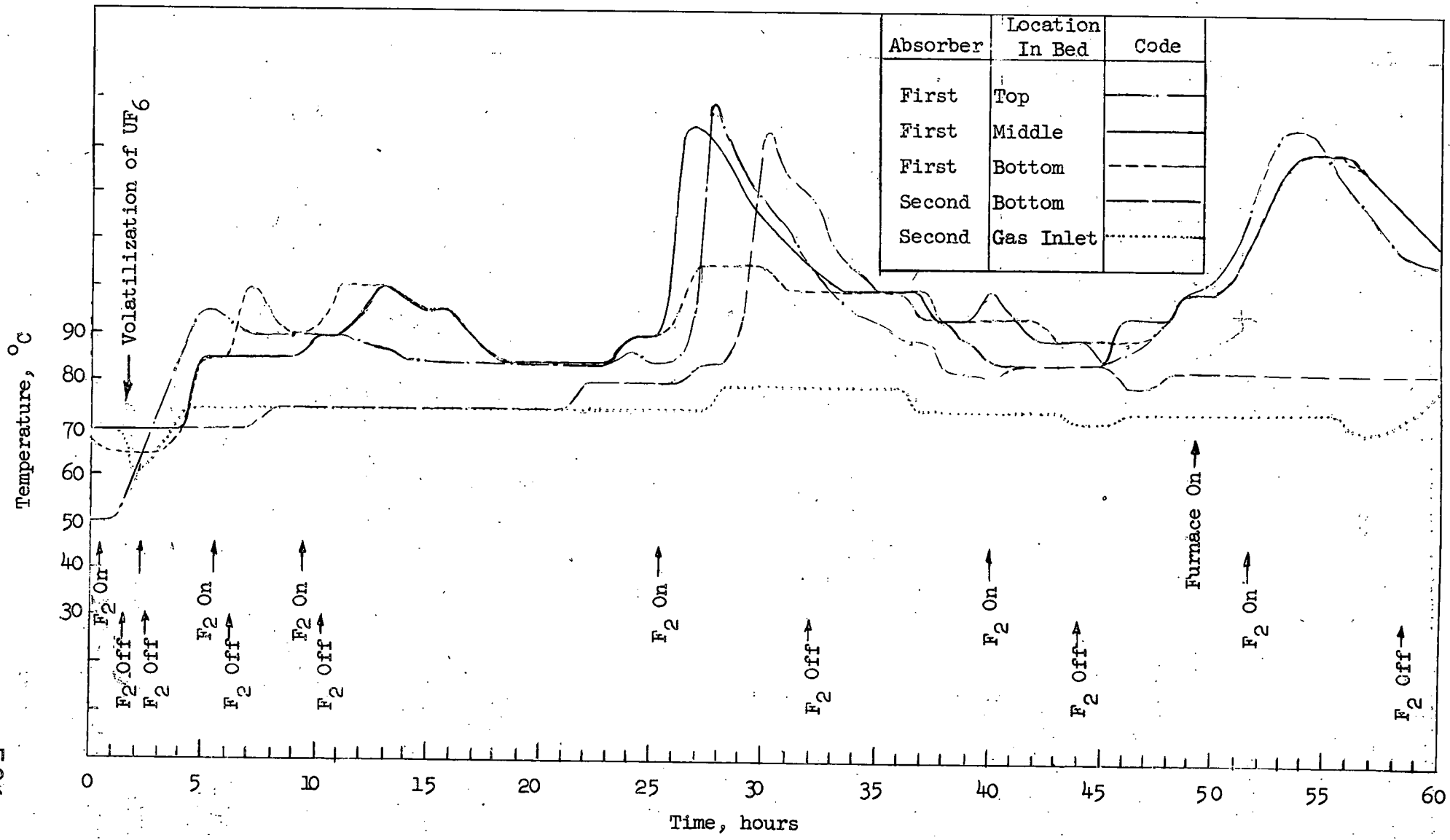Fig. 15.2. Temperatures in the Absorbers during Absorption of UF$_6$ in Run E-1

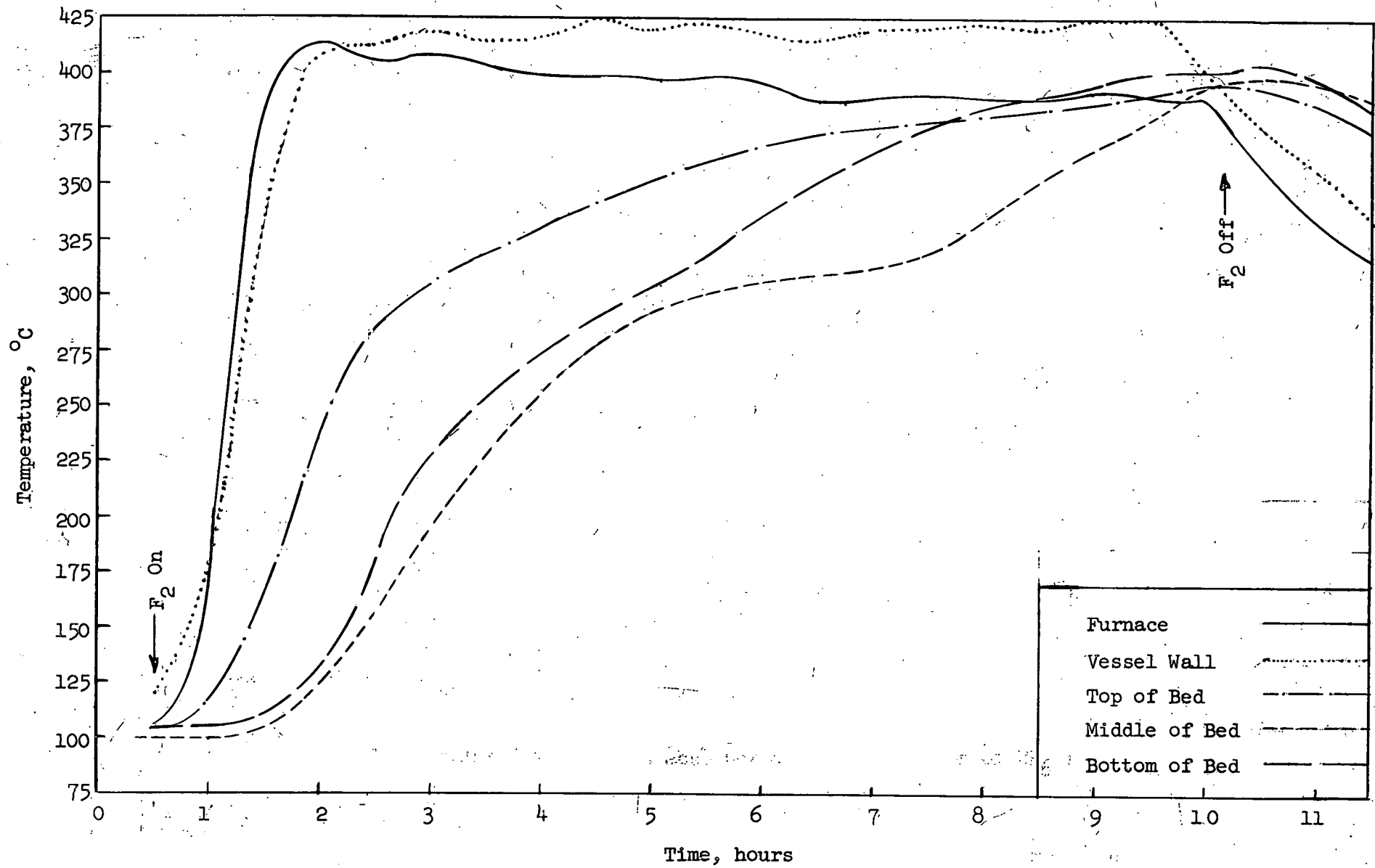Fig. 15.3. Temperatures in the Absorbers during Absorption of UF_6 in Run E-2

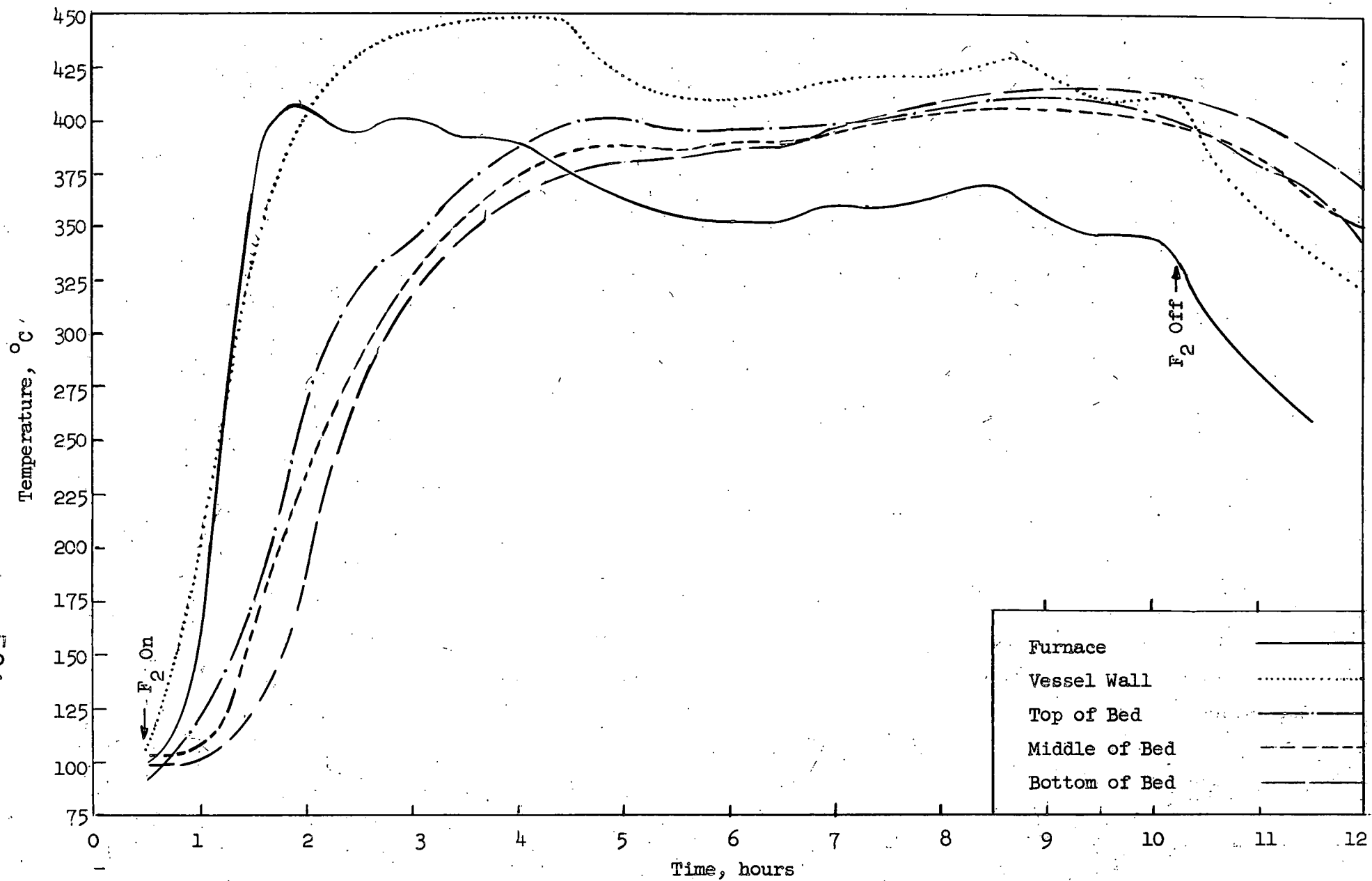Fig. 15.4. Temperature in the first absorber during Desorption of UF_6 in Run E-1

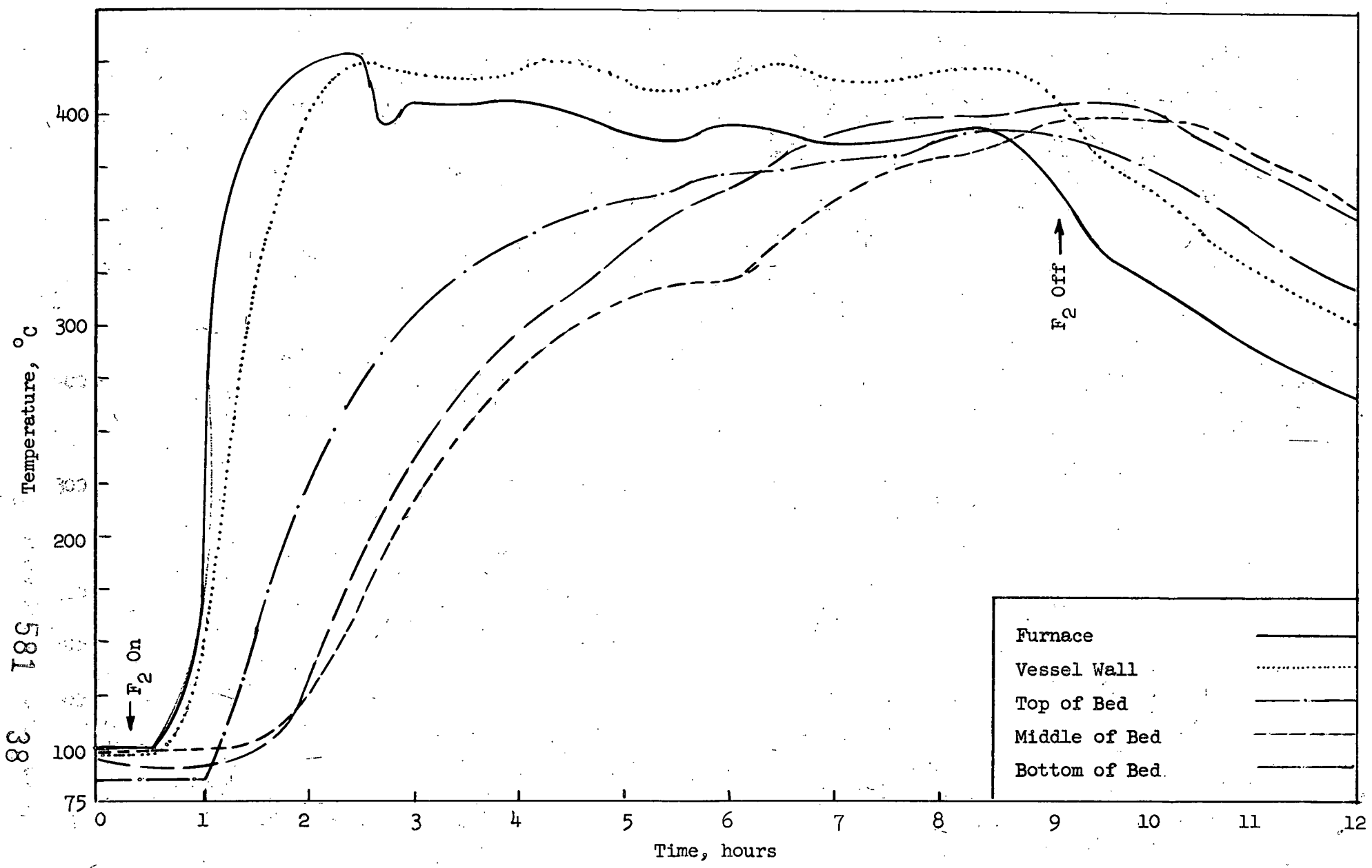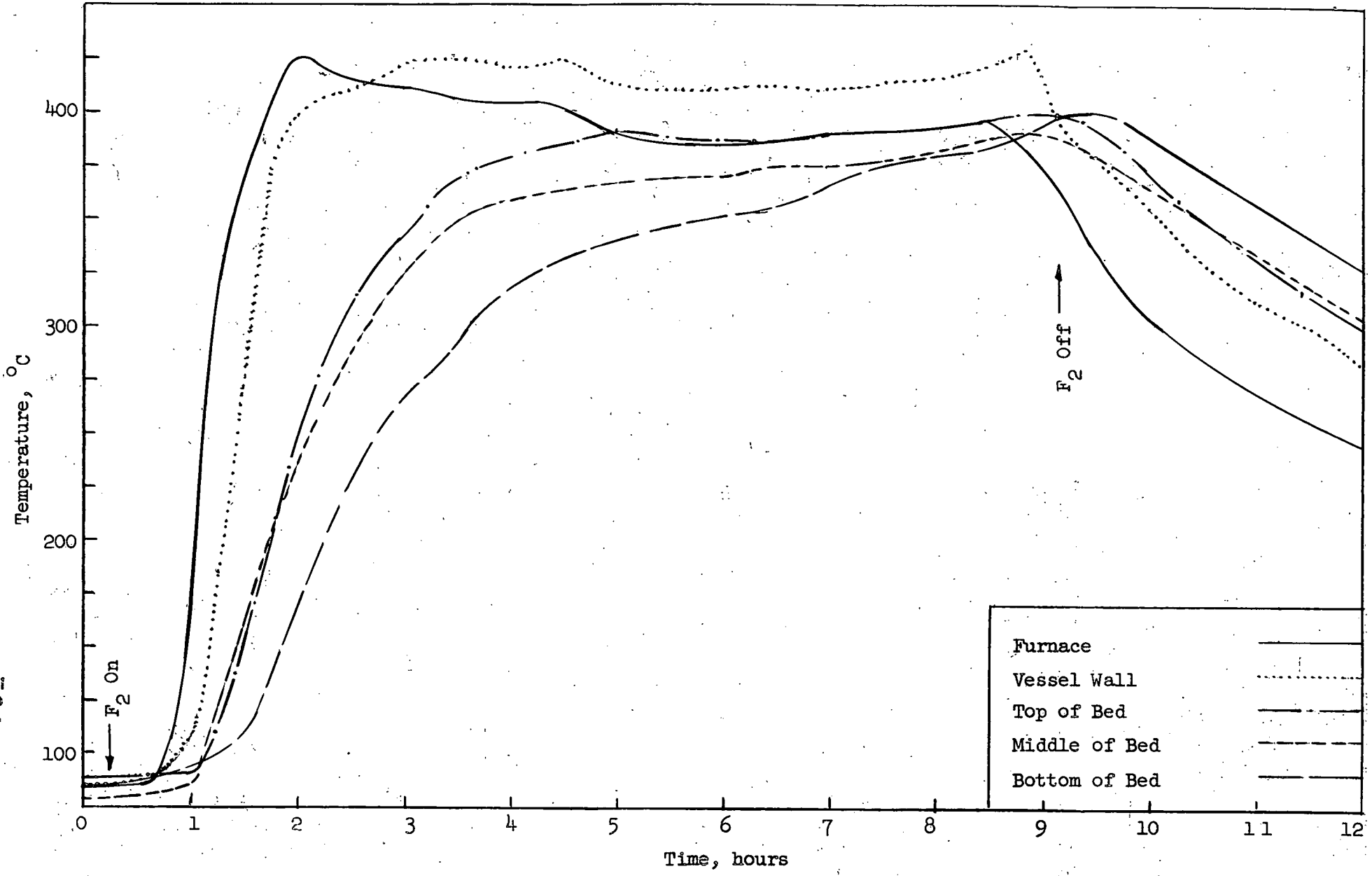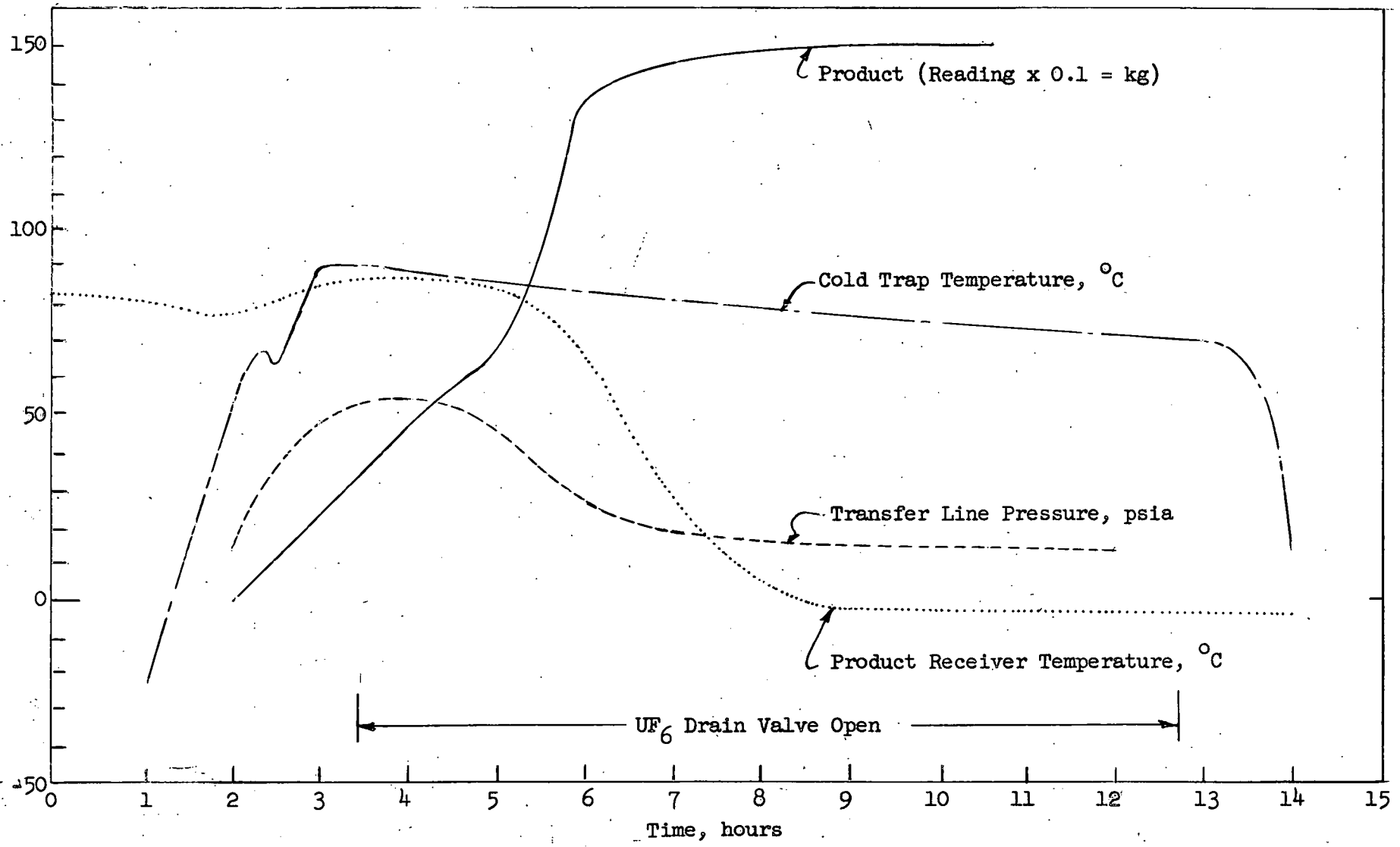Fig. 15.5. Temperatures in the Second Absorber during Desorption of UF$_6$ in Run E-1

Fig. 15.6. Temperatures in First Absorber during Desorption of UF_6 in Run E-2

Fig. 15.7. Temperatures in the Second Absorber during Desorption of UF_6 in Run E-2

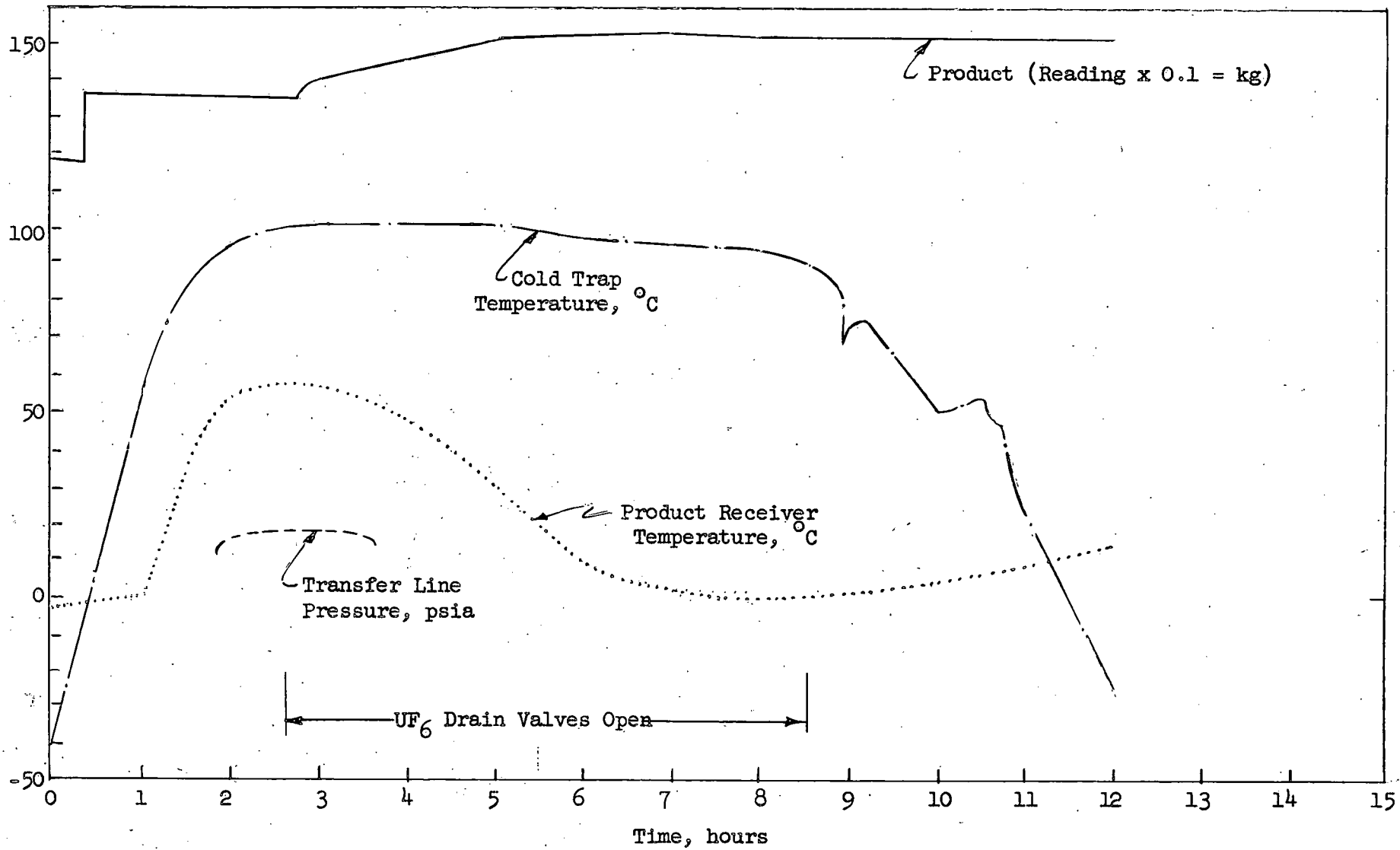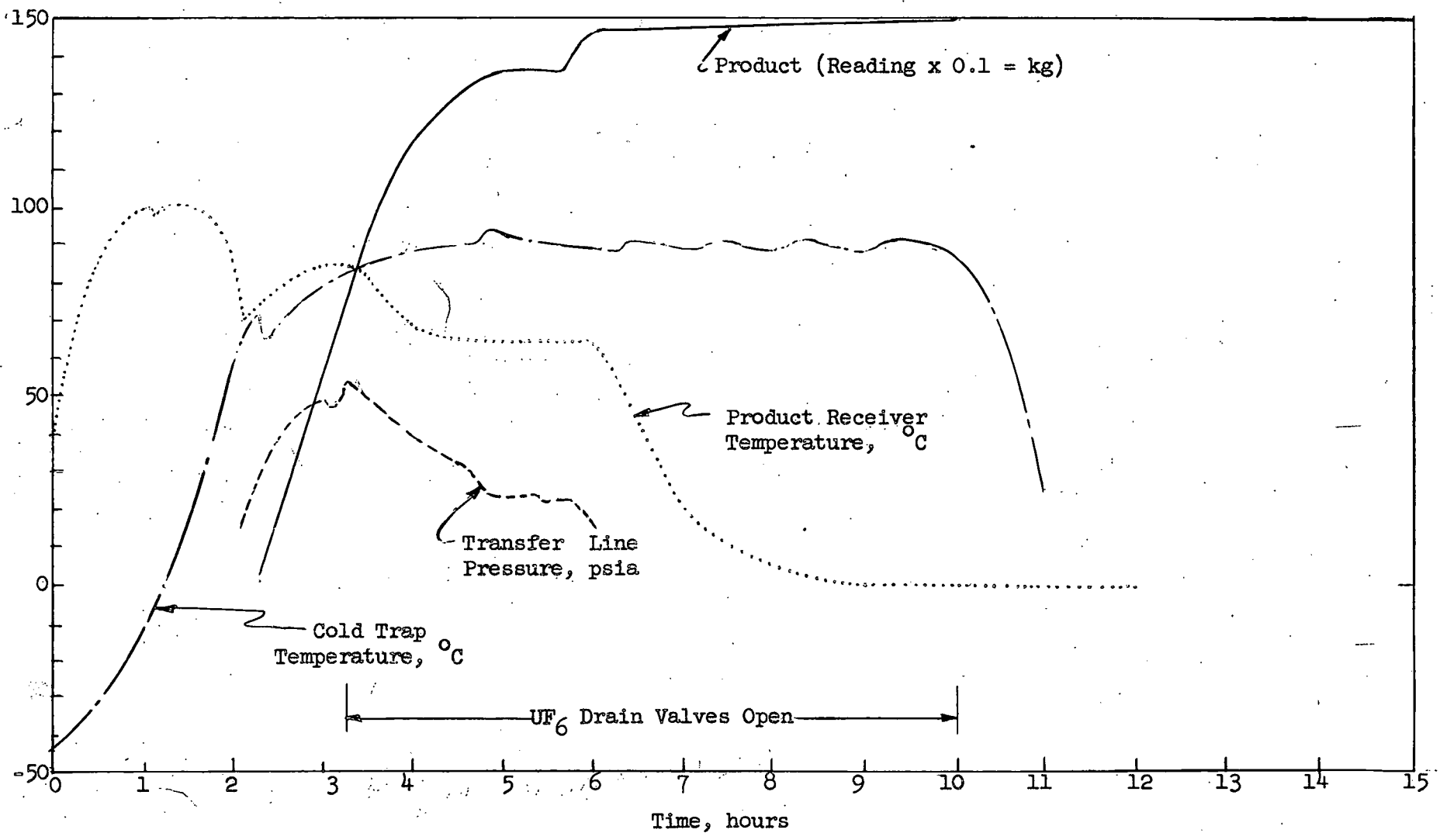Fig. 15.8. Product Transfer Conditions in Run E-1 (First Attempt)

Fig. 15.9. Product Transfer Conditions in Run E-1 (Second Attempt)

Fig. 15.10. Product Transfer Conditions in Run E-2

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