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FUSED SALT FUEL PROCESSING IN THE ORNL VOLATILITY PILOT PLANT

C. L. Whitmarsh
W. H. Carr

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CHEMICAL TECHNOLOGY DIVISION

Pilot Plant Section

FUSED SALT FUEL PROCESSING IN THE ORNL VOLATILITY PILOT PLANT

C. L. Whitmarsh and W. H. Carr

Date Issued

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ABSTRACT

A pilot plant development program was carried out for the Fluoride Volatility process, in which UF_4 contained in a mixture of molten fluorides is fluorinated to the volatile UF_6, which is further decontaminated by sorption-desorption in fixed NaF beds. The recovery, as UF_6, of ~134 kg of fully enriched uranium represented 97.93% of that in the feed, with an additional 1.76% being reclaimed from the NaF and in equipment cleanout; measured losses were 0.03%. The 0.28% unaccounted for may be attributed to an observed, but unmeasured, leak. The UF_6 product analyzed >99.5% of theoretical uranium concentration and contained about 500 ppm of total cation impurities. Since no fission product activity was detected in the product, plant-scale decontamination factors were not determinable. The activity of the material processed was only 10^5 gross gamma counts/min/mg U.

The chief difficulties, which decreased with experience, were plugging of molten salt lines, the maintaining of a gastight system, and plugging of the NaF beds. Corrosion, though greater than normal in chemical processing plants, did not limit operation.

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1.0 INTRODUCTION

This report describes the pilot plant development of the ORNL Fluoride Volatility process, which is based on the high volatility of uranium hexafluoride and the relatively low volatility of the fission product fluorides. Uranium tetrafluoride dissolved in a mixture of molten fluorides is fluorinated to the volatile UF_6; the UF_6 is further purified by sorption on and desorption from sodium fluoride beds. Established methods for recovering uranium from spent nuclear reactor fuels are based on liquid-liquid extraction between aqueous and organic solvents. Various nonaqueous processes with certain inherent advantages have also been investigated. Preliminary laboratory-scale study[1] indicated that the ORNL Fluoride Volatility process has the advantages of low waste volume, low capital investment, high decontamination factors, and stability to radioactivity. The pilot plant development work included study of the fluorination reaction, absorber operation, operation of the complexible radioactive products trap, plutonium behavior, and uranium recovery from sodium fluoride absorber beds. From the Aircraft Reactor Experiment[2] fuel (a fluoride salt mixture containing UF_4) 62 kg of fully enriched uranium was recovered, and from similar nuclear reactor fuel 72 kg was recovered in a subsequent series of development runs.[3] Since only low-activity feed was processed, the feasibility of operation at high levels of radioactivity could not be established.

Since a process that can handle only fluoride salt reactor fuels is obviously limited in application, a head-end treatment to dissolve zirconium-clad fuel elements in molten salt is being installed in the pilot plant and subsequent operation will be directed toward processing of radioactive zirconium-uranium fuel elements containing highly enriched uranium.

2.0 FLOWSHEET

The Fluoride Volatility process reported here is designed to recover uranium from molten salt reactor fuels by making use of the volatility of UF_6. For the purpose of discussing the flowsheet the process can conveniently be separated into (1) the molten salt handling system and (2) the UF_6 handling system (Fig. 2.1).

The pilot plant is designed[4] for a batch process, each batch consisting of 50 liters of salt containing ~10 kg of uranium. A batch of molten salt (NaF-ZrF_4-UF_4, m.p. ~525°C) is transferred to a reactor vessel (fluorinator) and maintained at 600°C. The UF_4 is oxidized to the volatile hexafluoride [UF_4 (liq) + F_2 (gas) → UF_6 (gas)↑] when elemental fluorine is added to the melt. The fluorination reaction is characterized by three periods: (1) an induction period during which there is no gas evolution from the melt, i. e., the fluorine is completely reacted and/or absorbed; (2) a period of UF_6 volatilization; and (3) a final period near the completion of the reaction when unreacted fluorine breaks through the melt. After completion of fluorination the waste salt, which contains >90% of the fission products, is pressure-transferred to a waste can and is subsequently transported in a shielded carrier to a disposal area.

In addition to UF_6, the gas leaving the fluorinator contains ZrF_4, volatile corrosion and fission product fluorides, entrained salt, unreacted

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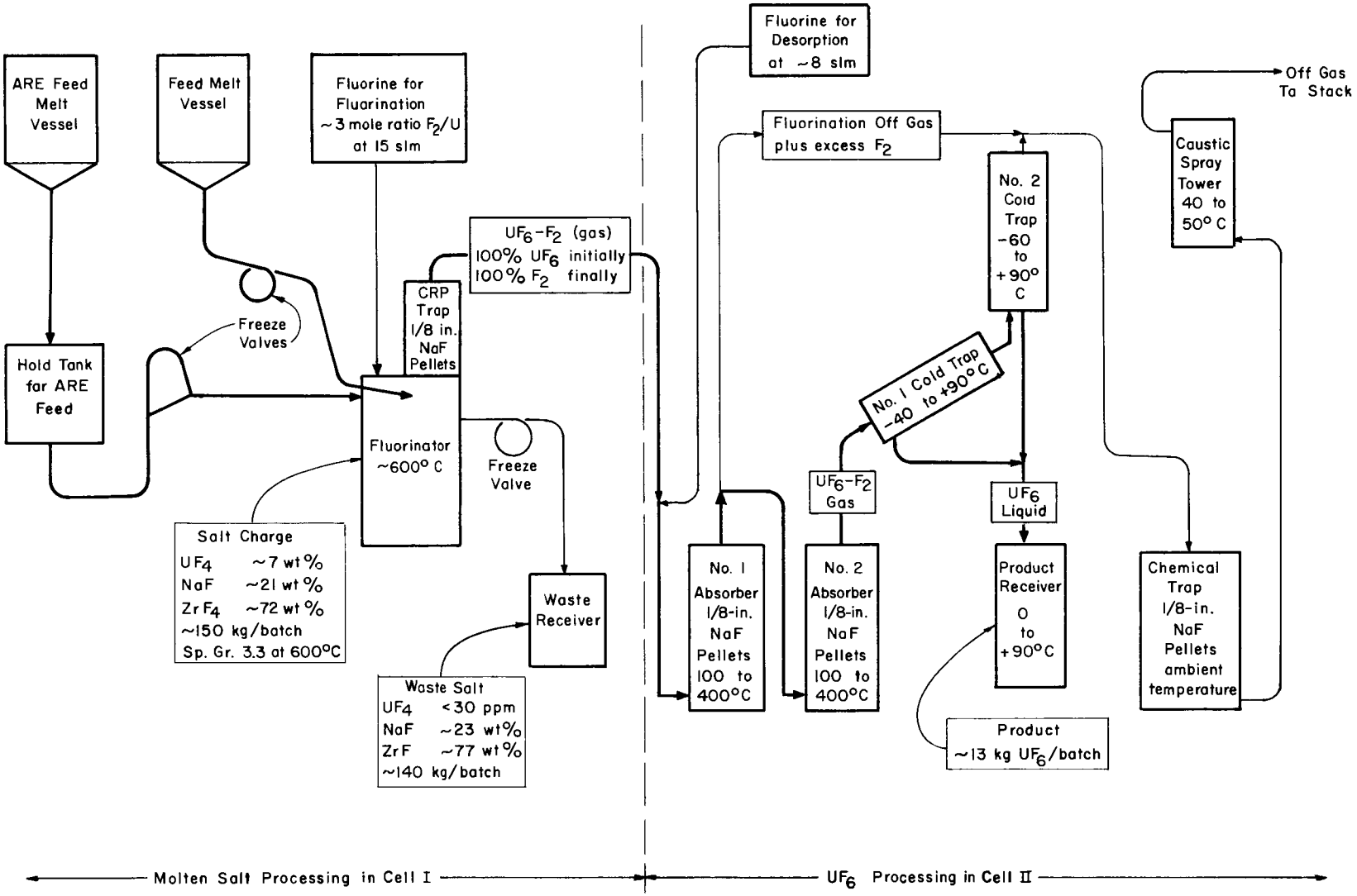

Fig. 2.1. Flowsheet for ORNL Fluoride Volatility Pilot Plant.

fluorine, and nitrogen. These gaseous products are routed through a bed of sodium fluoride (Complexible Radioactive Products trap) maintained at 400°C to separate out the zirconium tetrafluoride, entrained salt, and certain volatile fluorides by sorption and/or filtration. The gas is then passed through the first absorber, a fixed bed of sodium fluoride pellets at ~100°C, where the UF_6 and most of the remaining fluorides are sorbed ($UF_6 + 3NaF \longrightarrow UF_6 \cdot 3NaF$, $\Delta H = -23.2$ kcal). The gas stream is then routed through a chemical trap, a fixed bed of sodium fluoride pellets at ambient temperature to remove any residual UF_6, and a caustic spray tower to neutralize excess fluorine.

After fluorination and sorption are complete, the UF_6 is desorbed from the sodium fluoride, leaving the other materials on the bed. This is accomplished by heating both absorber beds simultaneously to 400°C in an atmosphere of fluorine sweep gas maintained at the lowest convenient rate. Excess fluorine is necessary to prevent any reduction of UF_6 to nonvolatile UF_5. The second absorber decontaminates the UF_6 from any volatile fission product fluorides, which would tend to leave the first absorber during desorption. The UF_6, after passing through both absorbers, is desublimed in two cold traps arranged in series. The first, operated at -40°C, retains the bulk of the UF_6 whereas the second, at -55°C, serves as a backup. The chemical trap and fluorine disposal system serve the same purpose as in the fluorination-sorption step.

The cold traps and the piping system leading to the product cylinder are isolated from the rest of the system and then evacuated to an absolute pressure of ~0.5 mm Hg. This part of the system is heated above the UF_6 triple point (64°C and 7 psig), thereby liquefying the UF_6 in an atmosphere of UF_6 vapor. Then the liquid is drained to a product cylinder, a standard 5-in. UF_6 shipping cylinder. After all liquid has drained, the product cylinder is cooled to 0°C to effect a thermal transfer of UF_6 vapors. When thermal transfer is considered complete, the cylinder valves are closed and the cold traps are cooled to normal operating temperatures. Thus, any UF_6 not transferred is recondensed in the cold traps and retained for the next run.

The flowsheet was adjusted at times to fit special situations. Throughout the ARE and subsequent development runs the gas stream from the fluorinator during fluorination was routed through both absorbers in series. This provided a second sodium fluoride bed to sorb the UF_6 in the event that it broke through the first bed as the result of overloading and/or channeling. The use of both absorbers was permissible because of the absence of any significant quantity of Ru-106 and the over-all low activity level of the feed.

The feed salt for the last series of development runs had a uranium concentration almost double that for which the process was designed, i. e., a 50-liter batch contained ~20 kg of uranium. Therefore the processing of this salt was begun on the basis that two runs would be required to remove all the uranium from one batch of salt. About 10 kg of uranium would be fluorinated in the first run, and the remaining uranium would be fluorinated from this same batch of salt in the following run. However, this method had to be abandoned after four runs due to nickel fluoride buildup in the salt. The nickel fluoride exceeded the solubility limits and plugged all molten salt transfer lines connected to the fluorinator (Sec. 5.3). Each remaining

run in this series was made with a feed consisting of one-half uranium-bearing salt plus one-half barren salt (50-50 mole % $NaF-ZrF_4$).

Only in the final run of a series was the waste transfer carried to completion. In all preceding runs a heel of ~15 kg of salt was left in the fluorinator to provide the necessary volume adjustment for the next batch of feed salt and to prevent "blowing" of the seal in the waste transfer line freeze valve.

3.0 URANIUM RECOVERY

Of a total of 133.9 kg of uranium fed to the system, 97.93% was recovered as UF_6 product. An additional 1.76% was recovered in the form of aqueous solutions from dissolutions of sodium fluoride beds and equipment washes. Measured losses represented 0.03% and an additional 0.28% was unaccounted for (Table 3.1). The measured loss of 0.03% represents the chemical process loss.

Table 3.1. Uranium Material Balance

	Weight, g		
	ARE Series	Development Series	Total
Feed	61,629	72,278	133,907
Recovery			
UF_6 product	59,376	71,761	131,137
Trapped on NaF	983	481	1,464
Holdup	511	363	874
Miscellaneous (KOH solution)	14		14
Losses			
Waste salt	20	9	29
Miscellaneous (deposits on cell wall)	14		14
Accounted for			133,532

However, an operational error resulted in a major UF_6 leak during the ARE runs. This UF_6 leak was responsible for the major portion of the 375 g of uranium unaccounted for. The leak could not be measured quantitatively, but the material balance deficit at that time indicated the loss to be ~750 g of uranium. The 1.76% contained in aqueous solutions was recovered at another facility by aqueous processing methods.

The product met isotopic and fission product activity specifications for product UF_6 (Table 3.2). (Sampling and analytical techniques are included in the Appendix.) Total impurities, as measured by cation content, were excessive for UF_6 to be returned to the gaseous diffusion cascade. Chromium and copper were the two cations which most consistently exceeded

specifications for individual elements. However, subsequent reduction to green salt reduced the cation content to within specification limits for metallic uranium.

Table 3.2. Product Purity

Runs	Purity, %	Total Impurities,[a] ppm based on U	U Isotope, wt %				Activity[b]
			234	235	236	238	
ARE	99.55	500	1.17	93.05	0.32	5.46	None
Development series	99.68	500	0.97	93.30	0.33	5.40	None

[a]Cations detected by spectrographic analysis.

[b]Other than that attributed to uranium.

4.0 DECONTAMINATION

Pilot plant demonstration of decontamination from fission products was limited to six runs with long-decayed (~4 years) low-burnup material (ARE) and to one run spiked with shorter decayed material (1-3 years) in the subsequent development series. Essentially all gamma activity in the ARE salt resulted from Cs-137 whereas significant quantities of Nb-95 and Zr-95 were present in the shorter decayed material. In both cases fission product activity in the feed salt was only ~0.2 curie per batch.

With both types of feed the uranium was completely decontaminated from fission product activity. No activity other than that attributed to uranium was detected in the UF_6 product. For calculation purposes a gross gamma activity of 1 cpm/mg U in excess of uranium gamma was assigned to the product, and the resulting decontamination factor was 9×10^4. Obviously, this method makes the decontamination factor dependent on and limited by feed salt activity. Complete decontamination was due in part to the low concentration or complete absence of certain fission products which form volatile fluorides, i. e., Nb, Ru, Te, Mo, and I. All but Ru are short-lived, and had decayed. The Ru had apparently been depleted by plating out on metal surfaces during reactor or loop operation.

Decontamination factors associated with various parts of the process are listed in Table 4.1. As expected, greater concentrations of volatile fission product fluorides in the feed salt caused lower gross gamma decontamination factors during fluorination. Total rare earths, which do not form volatile fluorides, were retained in the waste salt.

Volatilized activity was due primarily to Nb-95. Fission products that escaped the fluorinator (by volatilization and/or entrainment) were sorbed on sodium fluoride beds and/or deposited in the lines (Table 4.2). During the spiked run about 15% of the niobium gamma activity volatilized during fluorination; of this, 97% was retained in the CRP trap, ~3% in the first absorber, and <1% in the chemical trap. The data also indicate that sodium fluoride at 400°C (CRP trap) was more effective in removing NbF_5 than CsF from the fluorination gases.

Table 4.1. Decontamination Factors in the Volatility Pilot Plant

	Gr γ	Nb γ	Zr γ	Cs γ	Gr β	TRE β
ARE runs (avg/run)						
Fluorination	560	a	a	b	4.5×10^3	2×10^4
CRP trap	1.7	a	a	b	1.6	2
Absorber	$\leq$100	a	a	b	$\leq$40	$\leq$5
Over-all	$\geq 9\times10^4$	a	a	b	$\geq 2.5\times10^5$	$\geq 2\times10^5$
Spiked run						
Fluorination	22	6	160	500	2×10^3	3×10^4
CRP trap	19	30	8	1.2	4.2	1.4
Absorber	$\leq$44	$\leq$20	$\leq$9	$\leq$120	$\leq$46	$\leq$8
Over-all	$\geq 9.2\times10^4$	$\geq 2\times10^4$	$\geq 1.1\times10^4$	$\geq 6.8\times10^4$	$\geq 4.1\times10^5$	$\geq 3.4\times10^5$

[a]Activity level too low for accurate measurement.

[b]Essentially equal to gross gamma.

Table 4.2. Activity Measurements in the Volatility Pilot Plant

	Activity, cpm/mg U per Run						
	Gr γ[a]	Gr β[a]	Cs γ	Nb γ	Zr γ	Ru γ	TRE β
ARE series							
Feed	9×10^4	2.5×10^5		<100	<60	<140	1.6×10^5
CRP trap	75	21	b	13			4
1st absorber	81	31	b	<1			4
2nd absorber	4	2	b	<1			-
Product	<1	<1					
Spiked run							
Feed	9.2×10^4	4.1×10^5	6.8×10^4	2×10^4	1.1×10^4	<40	3.4×10^5
CRP trap	3.9×10^3	150	25	3×10^3	61		3
1st absorber	220	46	115	98	9		8
2nd absorber	c	c	c	c	c		c
Main chemical trap	5	1		5			
Product	<1	<1					

[a]In excess of activity resulting from uranium.

[b]Spot checks indicated that >90% of the gross gamma was due to Cs-137.

[c]Analyses were inconsistent but were of the same order of magnitude as in the ARE runs.

5.0 PLANT OPERATION

5.1 Equipment

All process vessels for the Volatility Pilot Plant are contained in two concrete cells, 11 x 19 x 27 (cell I) and 20 x 19 x 27 ft high (cell II); adjacent areas are utilized for fluorine disposal, fluorine and nitrogen supply, and a control panelboard.[4] The molten salt handling equipment is confined to cell I and the UF_6 handling system is in cell II. The process was designed for all operations except fuel loading and product removal to be performed at the panelboard (Fig. 5.1).

The wide range of process conditions (temperature -60 to ~600°C, pressure 0.5 mm Hg abs to ~40 psig), the radioactivity of the feed, and the corrosive properties of the materials necessitated development of certain equipment features.

The fluorinator is a 14-in.-o.d. x 53.5-in.-high straight-side L-nickel vessel in which molten salt is reacted with fluorine gas (Fig. 5.2). Fluorine is introduced through a draft tube to achieve gas-salt contacting and to circulate the salt in the vessel. The lower 19 in. of the fluorinator is encased in an electric furnace, and the upper portion is wrapped with electrical resistance heating elements to provide the necessary temperature control. An Inconel liner is installed between the fluorinator and the furnace to contain any molten salt leakage.

On the top flange of the fluorinator is a CRP (complexible radioactive products) trap. This is a 5-in.-i.d. x 33-in.-high vessel packed with ~7 kg of 1/8-in. NaF pellets (Fig. 5.2). The trap is wrapped with resistance heaters and 2 in. of insulation to provide the operating temperature of 400°C. The gas inlet and outlet were designed to minimize plug formation from deposition of zirconium tetrafluoride. A bypass line is provided in case the outlet or the bed does become plugged.

The two absorbers are identical vessels, 10 in. o.d. x 33 in. high, packed with ~26 kg of 1/8-in. NaF pellets and 14 kg of 1/4-in. nickel shot (Fig. 5.3). The nickel shot is placed in the bottom 4 in. of the vessel to cover the gas inlet and thus provide an inert medium for gas dispersion prior to exposure to the reactive (sodium fluoride) portion of the bed. The entire vessel is enclosed in an electric furnace and is provided with a compressed air supply directed between the furnace and the vessel for cooling during sorption of UF_6.

Two cold traps, operated at -40 and -55°C respectively, are connected in series to freeze out (desublimate) the UF_6 from the carrier gas. The first, or primary, cold trap is an 8-ft 8-in. length of 5-in. SPS deoxidized copper pipe provided with an internal arrangement of baffles (Fig. 5.4). The second cold trap is a 5-ft 4-in. length of 6-in. NPS Schedule 40 Monel pipe provided with cross baffles designed to operate in a vertical position (Fig. 5.5). Each trap is heated by resistance heaters and cooled by forced flow of Freon 11. Both traps are also equipped with vacuum jackets for insulation, leak checking, and containment of any leakage.

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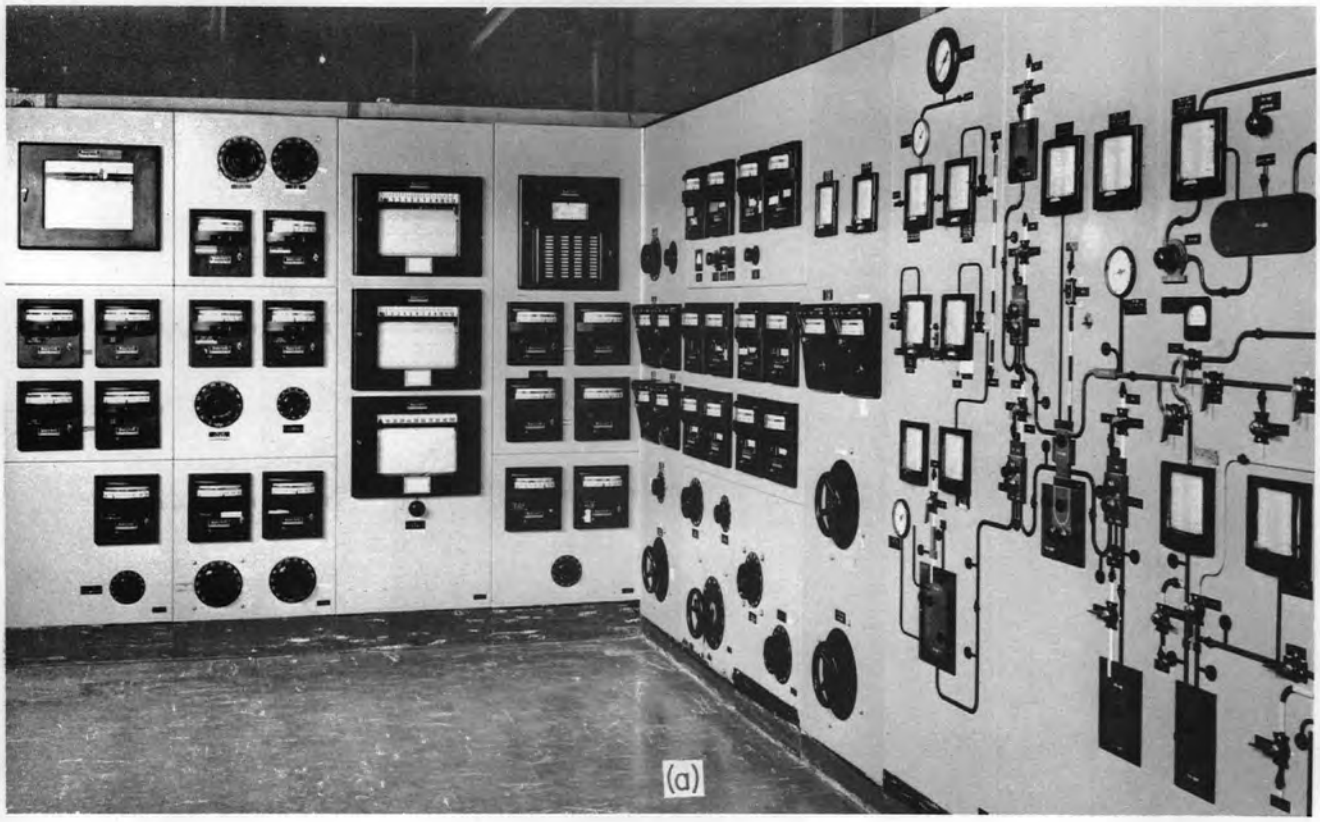

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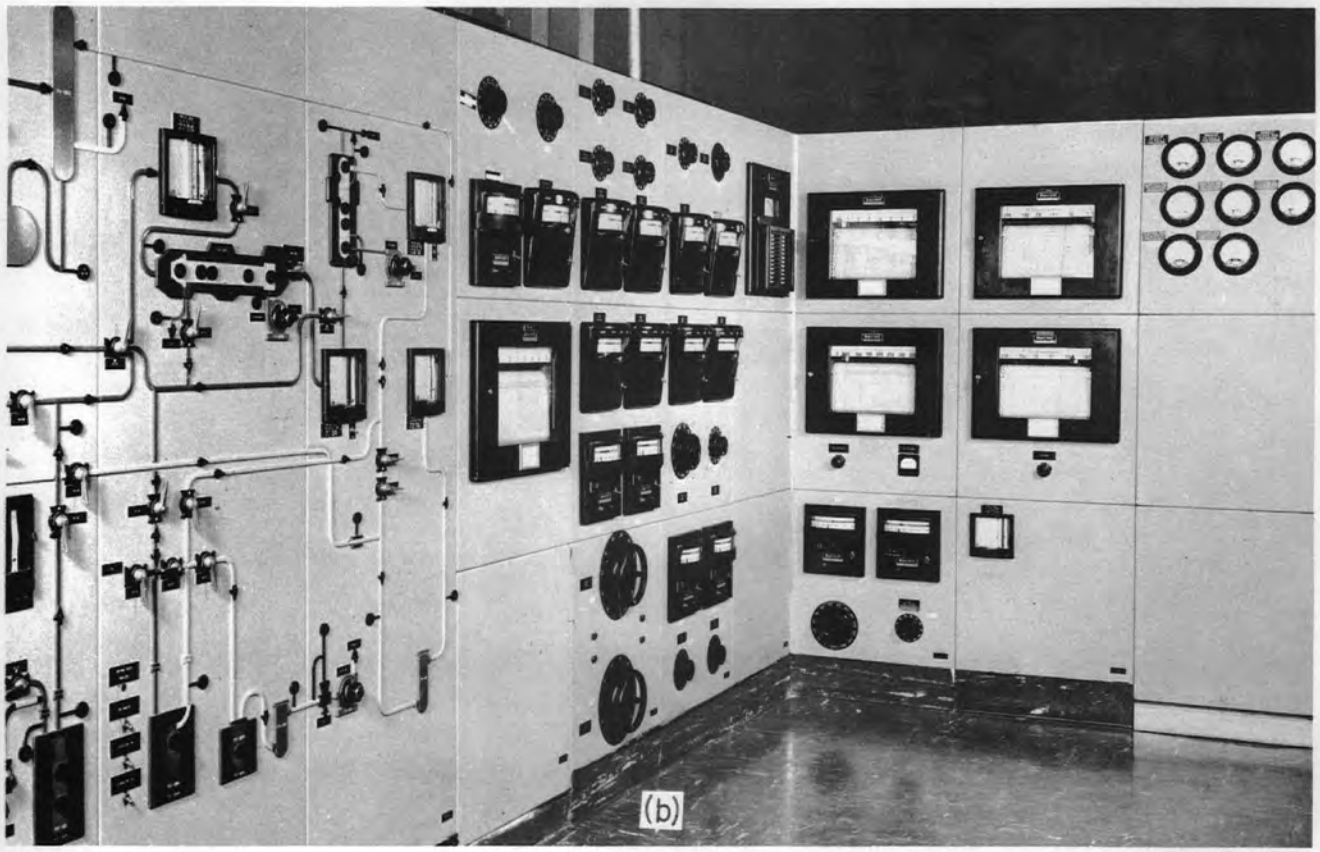

Fig. 5.1. Operating panel, (a) east half, (b) west half.

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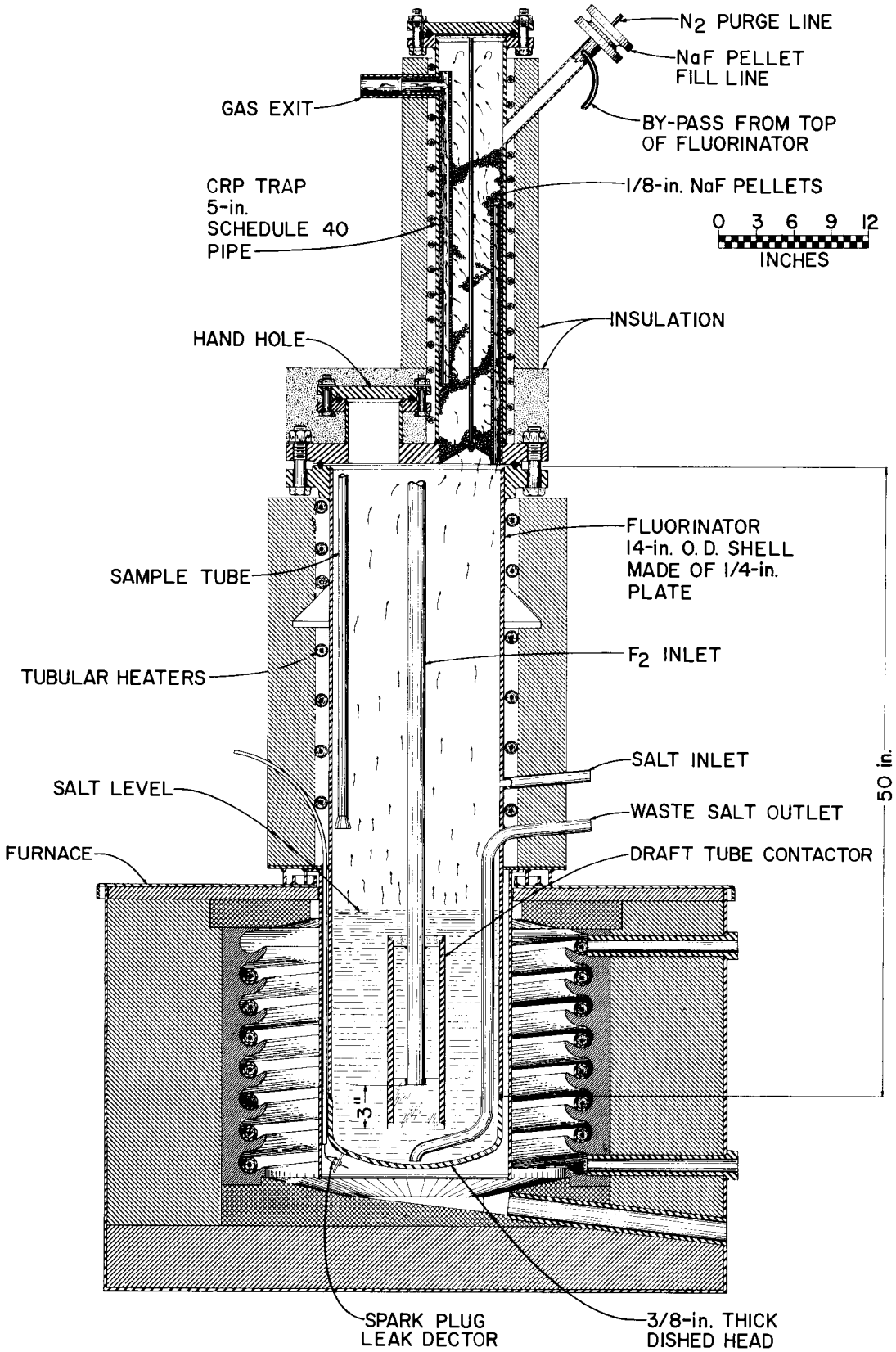

Fig. 5.2. Fluorinator, CRP trap, and furnace.

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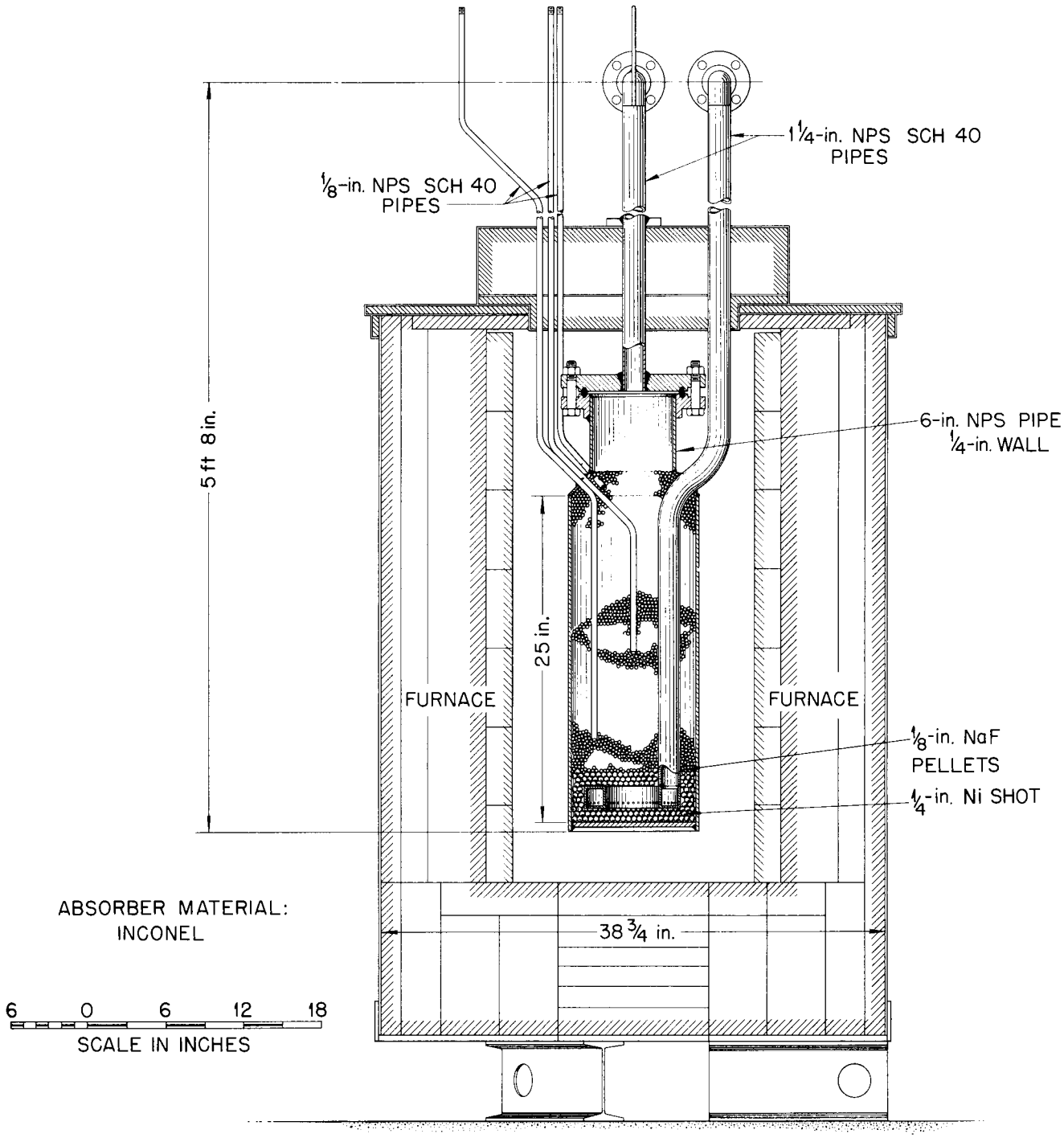

Fig. 5.3. Absorber and furnace.

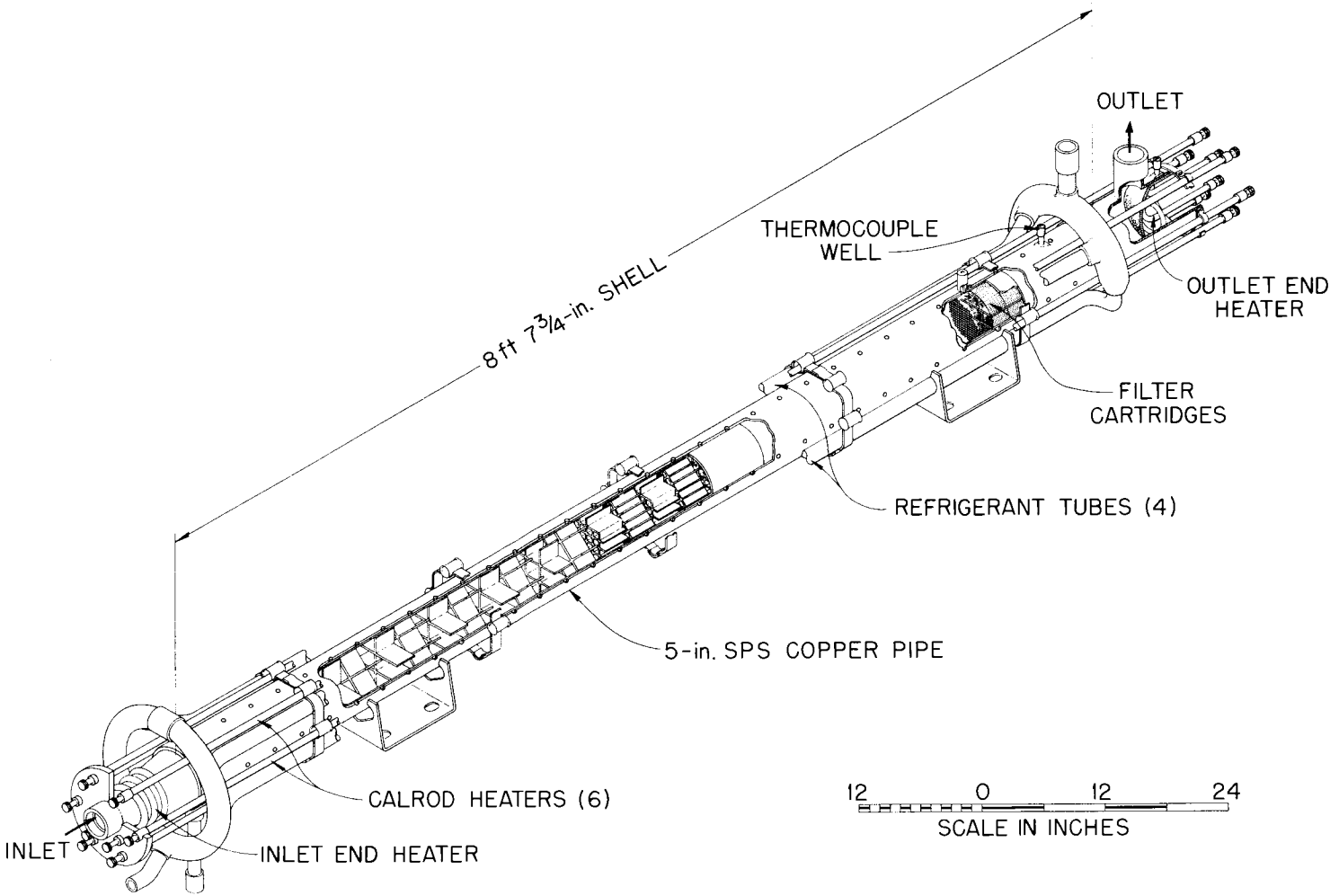

Fig. 5.4. Number one cold trap.

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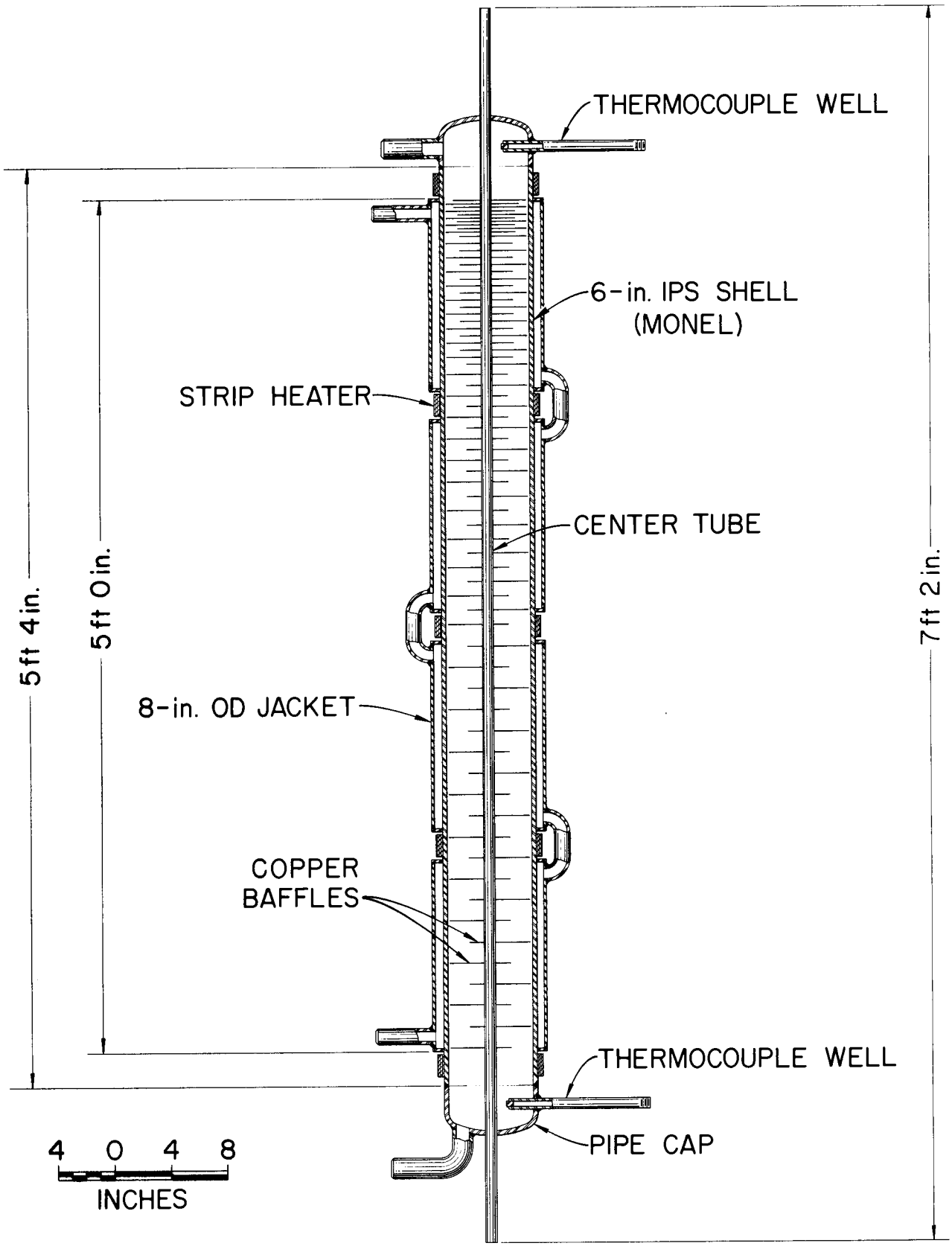

Fig. 5.5. Number two cold trap.

Fluorine disposal is accomplished with a spray tower fabricated from Monel, 12 in. o.d. x 10 ft high, in which the off-gas is reacted with an aqueous solution of ~10% KOH (Fig. 5.6). The caustic solution is circulated through the tower and a surge tank by an auxiliary pumping system.

Three chemical traps are included in the Volatility Pilot Plant. These are fixed beds of sodium fluoride pellets operated at ambient temperature, which are installed to prevent UF_6 from escaping from the system. The main trap is downstream from the second cold trap on the main process line; another is connected to the exhaust on the heated duct system; and the third is directly upstream from the vacuum pump used to evacuate the product system.

All lines through which molten salt flows are 3/8 or 1/2 in. NPS Schedule 40 Inconel pipe. These lines are heated by "autoresistance" heating, i. e., heat generated by passing an electric current through the pipe, and are wrapped with 2 in. of diatomaceous silica-asbestos fiber insulation. The UF_6 lines (Monel pipe) are enclosed in a heated duct system to prevent UF_6 deposition and to contain any leakage. The air temperature in the ducts is maintained at ~100°C by tubular electric heaters.

To obtain gastight seals in molten salt lines, freeze valves were used (Fig. 5.7). This valve is merely a loop, provided with vents, in the molten salt line in which salt can freeze. Several modifications of this valve have been used successfully,[5, 6] e. g., during ARE processing the feed line freeze valve was essentially a jack leg with a bypass.

Two types of remotely operated air-head valves were used in the UF_6 handling part of the system: (1) all Monel, metal-to-metal seat and disk, bellows sealed, and (2) Monel to Kel-F, bellows sealed. Both proved acceptable under operating conditions.

Instrumentation in the Volatility Pilot Plant included iron-Constantan thermocouples (-60 to 0°C), Chromel-Alumel thermocouples (0 to 700°C), strain gages, orifice type flow meters, pressure elements, specific gravity indicators, and level indicators. All instruments except thermocouples and strain gages were pneumatic with a 3 to 15 psig transmitter signal. Principal process control instruments were connected to recorders on the panelboard.

Pilot plant equipment is described in detail elsewhere.[7]

5.2 Operating Techniques

During the pilot plant operation various techniques were established to evaluate the progress of a run.

Progress of the fluorination reaction is followed by temperature and density measurements. The density of the salt starts decreasing when UF_6 is evolved from the melt and continues to decrease until all the uranium has been volatilized. Generally, fluorine flow into the melt is continued for at least 30 min after the salt density reaches a minimum to ensure complete reaction. Fluorine breakthrough, i. e., unreacted fluorine passing through the melt, is indicated by an increase in gas flow downstream from

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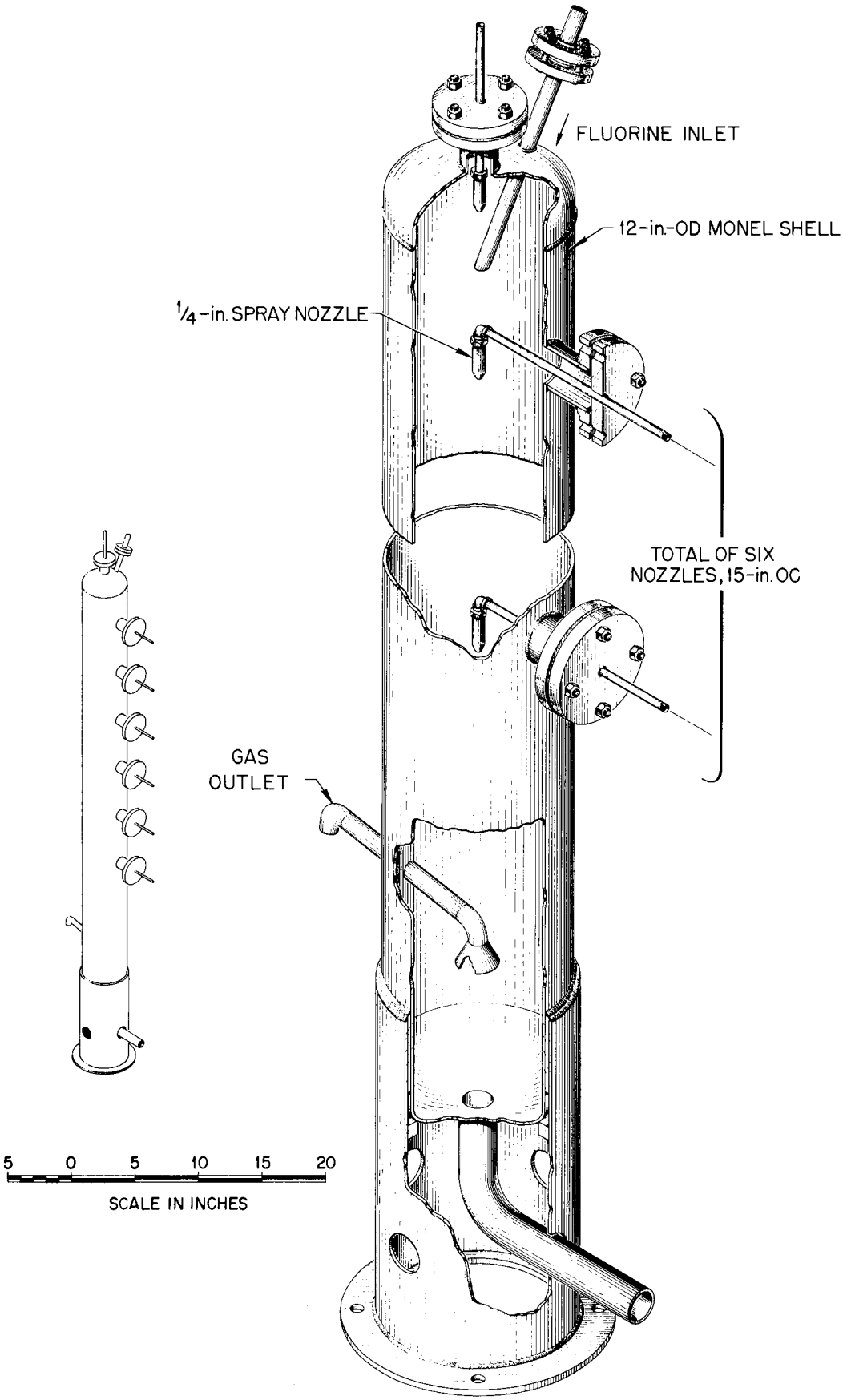

Fig. 5.6. Fluorine disposal spray tower.

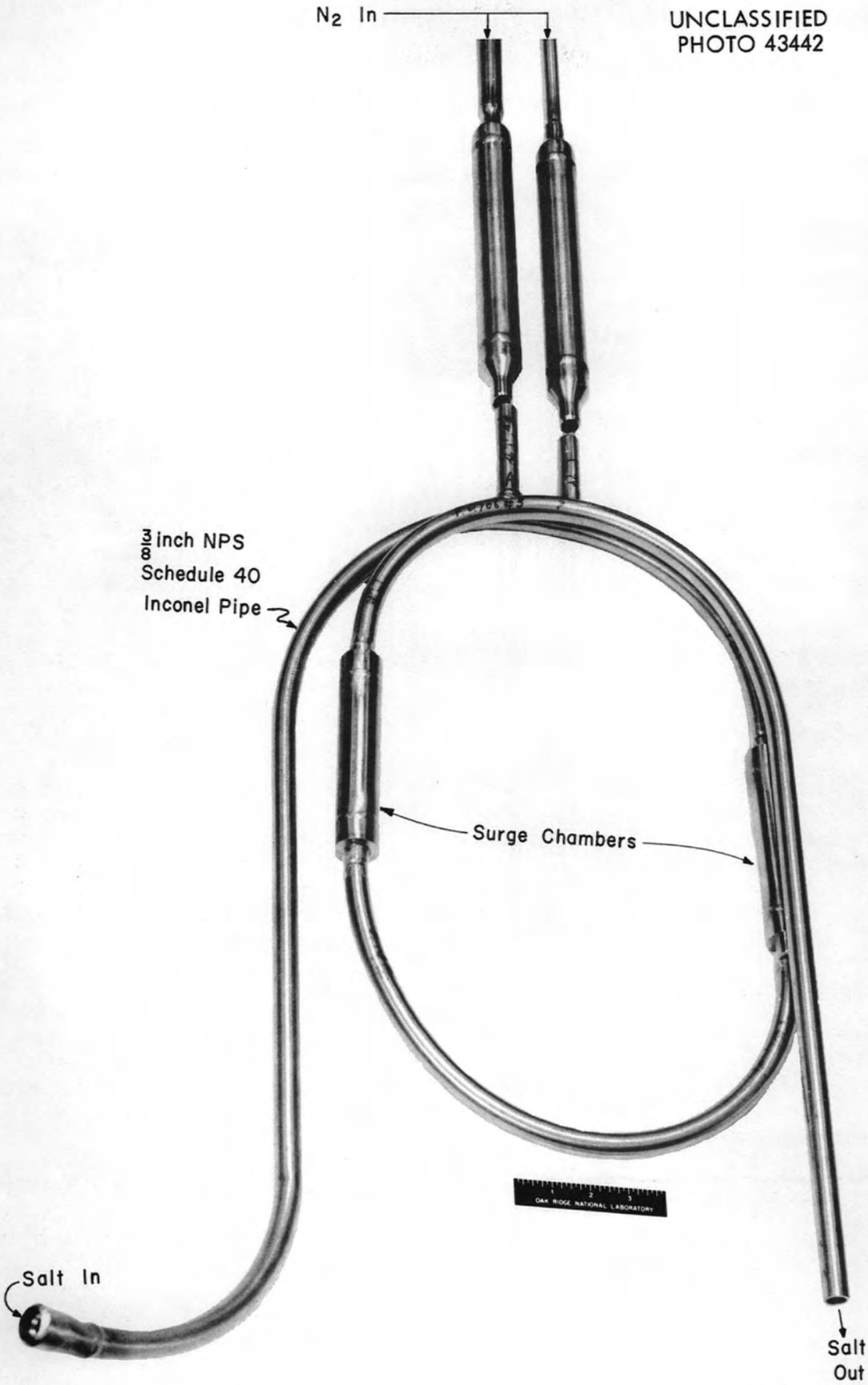

Fig. 5.7. Waste salt line freeze valve.

the fluorinator and a temperature increase (~20°C) of the caustic solution in the spray tower.

Although the reaction is estimated to be complete about 30 min. after the melt density has reached a minimum, the final decision to discontinue fluorination is reached after analysis of a salt sample. The salt can be transferred to the waste receiver when the uranium concentration is <25 ppm. This is an arbitrarily established value (and consequently is somewhat flexible) which represents >99.9% volatilization. During the waiting period of 1 to 2 hr required for analytical results, fluorine (~40 moles) is flowed into the melt for an additional hour and another set of waste salt samples is taken. This is done to conserve operating time in the event that analytical data indicate that the fluorination reaction was incomplete.

A temperature increase in the absorber bed indicates that UF_6 has reached that point and is reacting with the sodium fluoride. Thermocouples are situated at three levels in the bed, and the UF_6 loading region is indicated by the corresponding temperature. Gas enters the bed at the bottom, and generally there is little danger of UF_6 breaking through the bed until considerable loading occurs at the top, as indicated by the temperature at that point. Shortly after the bed temperature starts to increase, compressed air is directed against the absorber to minimize this rise.

Desorption of UF_6 is characterized by a plateau at 310-320°C in the curve of absorber bed temperature vs time. This indicates the period of maximum rate of desorption. Desorption is considered complete when all bed temperatures reach 390°C.

Uranium hexafluoride in the cold traps is transformed to a liquid when the temperature and pressure exceed 64°C and 22 psia, respectively. Generally, the temperature is increased to ~80°C (~43 psia) to ensure transformation. After the drain valves are opened, liquid UF_6 transfer is indicated by increasing weight of the product receiver and is considered complete when this weight becomes constant. Thermal transfer is then initiated and continued until the product receiver weight again becomes constant.

5.3 Operational Problems

Although pilot plant operation was considered reasonably trouble-free, a number of difficulties arose during the processing programs. From an operations standpoint the major recurring problems could be classified into three types: (1) plugging of lines with fluoride salt, (2) plugging of sodium fluoride beds, and (3) maintaining of a gastight system.

Line Plugs from Fluoride Salt. The single, most consistent difficulty encountered was plugging of lines in, or adjacent to, the fluorinator, e. g., molten salt transfer, fluorine inlet, and instrument lines. This caused interruptions in the run procedure because of (1) inability to transfer waste salt out of the fluorinator, (2) loss of fluorine supply for fluorination, or (3) loss of level and/or density instrumentation to follow the fluorination reaction. Generally, the plugs were removed by drilling out the salt or heating that section of line with hand-operated butane torches to melt the salt. However, in at least one case the salt had to be chipped

from the fluorinator with a pneumatic hammer. The seriousness of the situation becomes apparent when one realizes that because of personnel exposure none of these techniques would be feasible in radioactive operation.

Plugs usually formed when a pressure surge in the fluorinator forced molten salt into unheated sections of lines, where it then froze. These surges developed when valve operation occasionally caused the pressure in the vapor space of the fluorinator to exceed the static head of salt plus the nitrogen purge and/or the fluorine supply pressures. When the salt in these lines rose above the level of the melt, it froze because of the lower temperature ($\sim 450^{\circ}C$) of the vapor space. Experience indicated that the fluorinator could not be heated sufficiently high to melt these plugs.

Initially, the fluorine inlet line was most susceptible to plugging. Difficulties with this line were alleviated by an arrangement of two interlocked valves and an automatic pressure switch. These two valves, interlocked so that they were always in opposite positions, permitted equalization of the pressure in the fluorine supply line and in the fluorinator vapor space. Although normal operation was by manual control, the pressure switch was automatically activated if vapor space pressure exceeded 8 psig.

Plugs also formed as a result of precipitation of nickel fluoride sludge in the bottom of the fluorinator. During fluorination, corrosion of the nickel vessel resulted in a buildup of nickel fluoride in the melt (Sec. 6.1). If the concentration of NiF_2 exceeded 0.46 wt % at $600^{\circ}C$, a fine suspension was formed which settled very slowly to the bottom of the fluorinator. Since the final concentration was dependent on the quantity of nickel fluoride in the salt initially and the amount of buildup during processing, either or both of these factors could be used as a control measure. Trouble in the first four runs of the development series resulted from the use of the same batch of salt for two fluorinations, which caused extended exposure of the fluorinator vessel to partially fluorinated feed salt, and from high initial concentration of nickel fluoride. Subsequent dilution with barren salt, to lower the nickel fluoride concentration and to lower the uranium concentration so that one fluorination was sufficient per batch of salt, remedied the situation.

Cold spots in the autoresistance-heated system caused salt to freeze and plug transfer lines. The most difficult region to maintain at a molten salt temperature ($>550^{\circ}C$) was the outlet nozzle on the waste salt line, primarily because its shape was not amenable to resistance heating.

Plugging of Sodium Fluoride Beds. On numerous occasions gas flow through sodium fluoride beds was restricted, and sometimes completely cut off, during a run. If heat and/or nitrogen pressure failed to relieve the plug, the sodium fluoride bed was removed and replaced with fresh pellets. This required interruption of the run procedure, and manual operation which would result in personnel exposure if radioactive feed was being processed.

The chief source of this trouble was the CRP trap, the first sodium fluoride bed downstream from the fluorinator. Generally, the pressure drop across the bed showed a sharp increase with the initial exposure to UF_6. When removed, the pellets in the bed were somewhat agglomerated but could

be broken up by hand. Changing of the CRP trap bed during a run was quite troublesome because the salt in the fluorinator had to be frozen in order to reduce the temperature of the CRP trap and minimize the possibility of alpha contamination from UF_6.

Less CRP trap plugging was experienced after better temperature control was achieved. Below 320°C, UF_6 was retained in the trap and probably contributed to the plugging; at higher temperatures, impurities were sorbed by the sodium fluoride, which probably contributed to plugging by lowering the temperature required for sintering of the pellets. However, even with better temperature control, trouble was experienced if more than one run was attempted with the same sodium fluoride bed.

UF_6 Leaks. Because of the presence of volatile UF_6, a gastight system is imperative. Loss of UF_6 is undesirable from both accountability and biological hazard standpoints. Three major leaks occurred in the pilot plant, two during preliminary flowsheet demonstrations with depleted uranium and one during processing of the ARE fuel. The first was caused by a weld failure at a cold trap thermocouple well and the second by an incorrectly installed solenoid valve. The third one developed when UF_6 from the fluorinator backed up into a vent line, where it escaped through an improperly connected flange. In each case the leak was discovered visually when an operator was sent to investigate the lack of pressure in the system. Uranium hexafluoride reacts with moisture in the air to form a dense white smoke and quantities of less than 1 g can be seen easily.

After completion of the ARE run in which the UF_6 leak occurred, the plant was shut down for a complete leak test. The location of this leak (in a nitrogen line) demonstrated that all lines directly connected to the UF_6 system had to be subjected to strict leak control back to a bellows-sealed valve. All unnecessary fittings were eliminated, and a thorough, three-step, leak-testing program was set up. Each step was designed to detect progressively smaller leaks, and the testing methods conversely were more complex. A detailed description of leak-testing methods is given in the Appendix (Sec. 9.3).

5.4 Corrosion

Corrosion in the Volatility Pilot Plant may be evaluated in four categories: (1) fluorinator (molten fluoride salt, F_2, N_2, UF_6); (2) molten salt transfer system (molten fluoride salt, N_2); (3) UF_6 handling system (UF_6, F_2, N_2); and (4) fluorine disposal system (F_2, KOH, H_2O, KF). Only the first of these is considered serious for the present scale of operation.

The fluorinator, an L-nickel vessel with 1/4-in. sides and a 3/8-in. dished bottom (Sec. 5.1), contains molten salt which is sparged with fluorine to form volatile UF_6. Three distinct regions of corrosive attack occurred in the vessel: (1) vapor, (2) vapor-liquid interface, and (3) molten salt. Corrosion rates were determined by wall thickness measurements with an ultrasonic device and by metallographic examination of the sectioned vessel (Table 5.1). In every region the corrosion mechanism appeared to be a combination of intergranular attack and of metal loss by chemical reaction ($Ni + F_2 \longrightarrow NiF_2$), with subsequent dissolution of the nickel fluoride film in molten salt.

Table 5.1. Corrosion Rates in the Fluorinator

Region	Corrosion Rate, mils per month[a]	
	Shakedown Runs	Avg over Final 15 Runs[b]
Vapor space	33-46[c]	5-22[c]
Salt-vapor interface	17-23	18-45
Salt wetted area	21-26	41-60

[a]Based on exposure time to molten salt ($T > 550^{\circ}C$) and includes both metal loss and intergranular attack.

[b]Includes ARE runs and final development series.

[c]Range of measurements at various points on the vessel wall.

Some qualification of the "average" rate listed in Table 5.1 should be made. Ultrasonic and micrometer measurements indicated that essentially all the corrosion occurred during the first ten runs (six ARE and four development) and very little over the last five runs,[8] the major difference between the periods being the time of vessel exposure to partially fluorinated salt (Sec. 6.1).

Results from a series of tests to determine a material of construction for future fluorination vessels indicated that certain nickel-rich alloys containing iron, cobalt, and/or molybdenum had some promise as a replacement material for L-nickel.[8] Improvement was shown in resistance to intergranular attack. These tests involved exposure of rods of various materials to actual run conditions.

Other equipment exposed to molten salt include a hold tank, freeze valves, and transfer lines. During the ARE runs, a 347 stainless steel hold tank contained the reservoir of salt from which each batch was withdrawn. This vessel was exposed to molten salt at ~585°C under a nitrogen blanket for 2200 hr. Although a metallurgical examination has not yet been made, an indication of metal dissolution is given by chemical analyses of the salt batches (Table 5.2). The rate of stainless steel corrosion by metal dissolution does not appear to be significant. Corrosion of the Inconel freeze valves and transfer lines was not excessive.

Corrosion in the UF_6 handling system did not present a serious problem. The absorbers were constructed of Inconel, the cold traps were copper and Monel, and all piping was Monel. A loosely adherent scale formed on the interior wall of the absorbers and tended to flake off when the sodium fluoride beds were changed. Chemical analysis of the scale indicated it to be >75% NiF_2. There was no evidence of significant metal loss in these vessels.[9] Although the cold traps and piping were not examined critically, there has been no indication of significant corrosion in either area.

Table 5.2. Fluoride Salt Analysis after Contact with Stainless Steel

Run No.	Exposure Time at ~585°C, hr	Concentration, wt %[a]		
		Fe	Cr	Ni
E-1	171	0.0780	0.0560	0.017
E-2	210	0.0330	0.0440	0.036
E-3	1970	0.0509	0.0406	0.138
E-4	2041	0.0590	0.0458	0.0779
E-5	2114	0.0518	0.0382	0.0773
E-6	2187	0.0550	0.0311	0.0840

[a]Each batch was sampled after transfer to the fluorinator.

During normal operation the fluorine disposal system was also relatively free of corrosion. These vessels, fabricated from Monel, were subjected to exterior visual inspection and thickness measurements with an ultrasonic gage.[9] The gas inlet nozzle to the spray tower was severely corroded, but it is believed that this occurred during a pre-run test at elevated temperatures.

6.0 DEVELOPMENT STUDIES

6.1 Fluorination

The fluorination reaction

$$UF_4\ (liq) + F_2\ (gas) \xrightarrow{600^\circ C} UF_6\ (gas),\ \Delta H = -62\ kcal$$

has been studied on a laboratory scale[1] and in the pilot plant. This reaction can be separated into three distinct phases: (1) an induction period in which fluorine is added to the melt; (2) a period during which UF_6 breaks through the melt; and (3) a final period when unreacted fluorine appears in the off-gas from the melt (Fig. 6.1). The UF_6 breakthrough, fluorine breakthrough, and final uranium concentration have been established as performance criteria.

The fluorination data indicate that (1) 30-40 moles of fluorine was required to initiate UF_6 volatilization in pilot plant equipment; (2) UF_6 volatilization was essentially complete (fluorine breakthrough) after 2.0-2.5 moles of fluorine per mole of uranium was used; and (3) the uranium concentration could be reduced to <25 ppm by fluorination and volatilization (Table 6.1). The 30-40 moles of fluorine prior to UF_6 volatilization appeared to be reasonably constant and independent of the total uranium in the salt, as indicated by comparison with runs L-1, 2 and L-3, 4 in which the uranium content and concentration were a factor of ~2 greater than in all other runs. Since this amount of fluorine apparently was required to

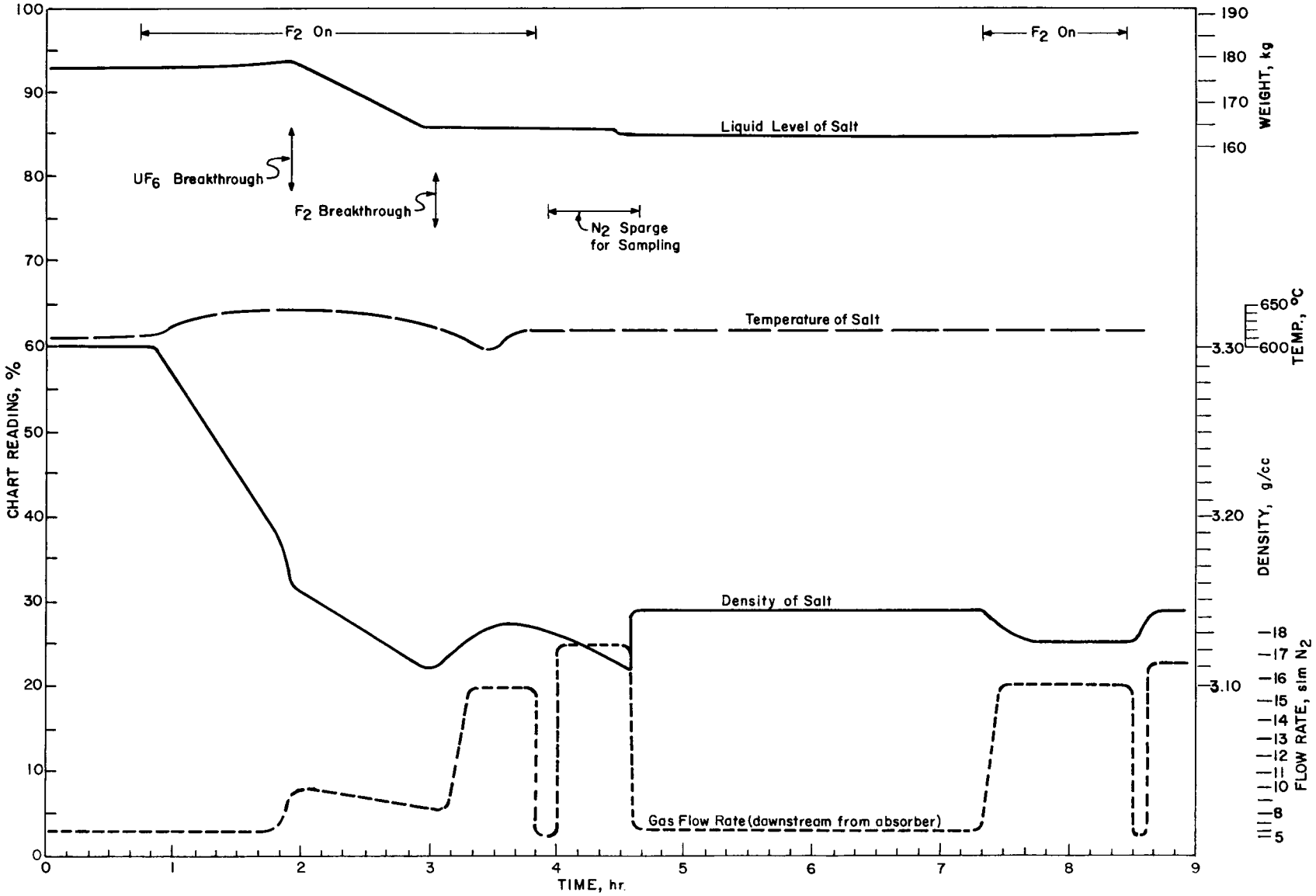

Fig. 6.1. Process conditions during fluorination.

Table 6.1. Fluorination Efficiency

Run	F_2 Rate, std liters/min	UF_6 Breakthrough, moles F_2 per initial mole U	UF_6 Breakthrough, moles F_2 Total	F_2 Breakthrough, moles per initial mole U	Total moles F_2[a] per initial mole U	Final U Conc., ppm	U Volatilized, % of initial
			ARE Runs				
E-1	13.1	0.66	30	2.0	2.9	80	99.87
E-2	4.8[b]	0.86	39	2.3	5.7	3	99.99
E-3	15.9	0.70	32	1.5	2.4	6	99.97
E-4	16.0	0.71	34	1.6	2.3	21	99.97
E-5	13.4	0.66	28	1.8	2.4	5	>99.99
E-6	13.3	0.73	26	1.9	2.9	27	>99.99
			Development Runs				
L-1, 2	15.3, 8.2[b]	0.63	42	2.7	5.1	41	99.97
L-3, 4	5.3,[b]6.3[b]	0.47	33	2.3	4.6	8	99.99
L-5	15.8	1.0	34	2.4	3.4	<1	>99.99
L-6	13.3	1.1	31	1.8	2.8	3	>99.99
L-7	15.6	1.0	42	2.2	2.9	3	>99.99
L-8	15.8	0.77	29	2.3	3.3	8	>99.99
L-9	13.5	0.94	26	2.2	3.1	1	>99.99

[a]Fluorine required to reduce the uranium concentration to an acceptable waste salt level, and not necessarily the total fluorine used in the run.

[b]Buildup of pressure in sodium fluoride beds necessitated decreased flow rates.

saturate the salt and convert impurities to their fluorides, it may be considered a function of total salt and impurities. Fluorine breakthrough, however, was a function of uranium content in the salt. Excessive total fluorine used in runs L-1, 2 and L-3, 4 may be related to excessive corrosion in these runs.

During flowsheet demonstration runs flow rates from 6.7 to 33.4 standard liters/min were investigated, with fluorine utilization and uranium recovery being the parameters for evaluation. The optimum fluorine flow rate for fluorination was determined to be in the range 10 to 30 standard liters/min.[10]

The reaction between fluorine and UF_4 appeared to be very rapid at 600°C, the main problem therefore being the contacting of fluorine gas with UF_4 liquid. For this purpose a draft tube contactor was used, which combined the advantages of simple design and maintenance-free operation with adequate mixing performance. Draft tube performance was optimum at a submergence of 1 to 2 in. In run L-8 fluorine was added to the melt through the waste salt transfer line during fluorination, thus affording a comparison between a dip tube (waste line) and the draft tube used in all other runs. In the pilot plant the reaction was insensitive to the change in contactors (Table 6.1).

Of the corrosion products and/or impurities in the melt, nickel and chromium fluorides are of most interest. Nickel fluoride builds up in the melt as a corrosion product of the fluorination reaction and precipitates as a fine suspension (Table 6.2). The higher fluorides of chromium (CrF_4 and CrF_5), which are volatile, leave the fluorinator and cause difficulty by (a) deposition on valve seats and/or (b) contamination of the product.

Table 6.2. Nickel Fluoride Solubility in Fluoride Salt[1]

Temperature, °C	NiF_2, wt %	Ni, wt %
640	0.7	0.4
670	1.0	0.6
685	1.3	0.8

Nickel fluoride precipitation was prevented by maintaining a feed analysis of <1000 ppm and limiting the exposure of a batch of salt to one fluorination period only. This latter restriction was not considered until runs L-1 through 4, in which a salt batch was exposed to two fluorinations (Sec. 2.0). During run L-4 nickel fluoride precipitated and plugged all the transfer lines. Subsequently, the salt was allowed to freeze and was chipped out with a pneumatic hammer. Both the initial nickel concentration (0.2 wt %) and the rate of the $Ni + F_2 \longrightarrow NiF_2$ reaction were greater than in previous runs (Table 6.3). Indications are that the corrosion rate was increased by longer exposure to molten salt containing partially fluorinated UF_4.

Fluorination of chromium is apparently dependent on uranium concentration, since chromium fluoride volatilization did not become significant until the uranium concentration was decreased to <0.03 wt % (Table 6.3). This suggests the possibility of regulating chromium fluoride volatilization by the extent of fluorination. At present the CRP trap (fixed bed of sodium fluoride) is installed primarily to remove chromium fluoride from fluorination gases (Sec. 6.3).

6.2 Absorbers

Gaseous UF_6 is decontaminated from volatile fission product fluorides, primarily NbF_5 and RuF_5, with lesser quantities of ZrF_4, by a sorption-

Table 6.3. Nickel and Chromium in Fused Salt during Fluorination at 600°C

Runs	Total Exposure to Molten Salt, hr	Total F_2, moles	Ni, wt %	Cr, ppm	U, wt %
L-1, 2	0	0	0.24	345	10.43
	41	79	0.63[a]	348	5.68
	127	206	-	287	0.0272
	133	334	0.61[a]	145	0.0040
L-3, 4	0	0	0.21	335	9.54
	148	87	4.5[a]	-	3.55
	172	187	2.0[a]	394	0.0356
	196	306	2.1[a]	170	0.0065
	210	327	1.1[a]	40	0.0008

[a]Not representative of melt because solubility limit was exceeded.

desorption reaction with sodium fluoride. The reaction

$$UF_6\ (gas) + 3NaF\ (solid) \underset{300\text{-}400^\circ C}{\overset{\sim 100^\circ C}{\rightleftharpoons}} UF_6 \cdot 3NaF\ (solid), \quad \Delta H = -23.2\ kcal$$

occurs in a fixed bed of sodium fluoride pellets contained in an Inconel vessel (Sec. 5.1). Two identical absorbers are in the system. Gas is routed to pass through the first absorber (maintained at <150°C) and bypass the second during fluorination and sorption of UF_6. Fluorides of uranium, niobium, and zirconium are complexed and retained by the sodium fluoride bed. Although ruthenium is unaffected by sodium fluoride at 100-200°C, a small fraction plates out on metal surfaces in the first absorber vessel. During desorption the beds are heated and gas is routed through both beds in series. At temperatures of 300-400°C uranium hexafluoride desorbs and passes through both beds whereas niobium and zirconium fluorides remain on the first bed and ruthenium fluoride carried over from the first vessel is retained in the second.[1]

The activity distribution in the first absorber after the spiked runs is shown in Fig. 6.2. Essentially all radioactive fission products were retained on the first 40% of the bed. The resulting gross gamma decontamination factor was ~200 and was apparently limited only by the quantity of activity. Considerably more Cs-137 reached the absorber than was expected.[11] Since cesium fluoride is nonvolatile, the transport mechanism was apparently entrainment. Essentially all gamma activity detected downstream from the absorbers was Nb-95.

Some uranium remained on the absorber beds after desorption. This was attributed to formation of nonvolatile UF_5. At temperatures >245°C the

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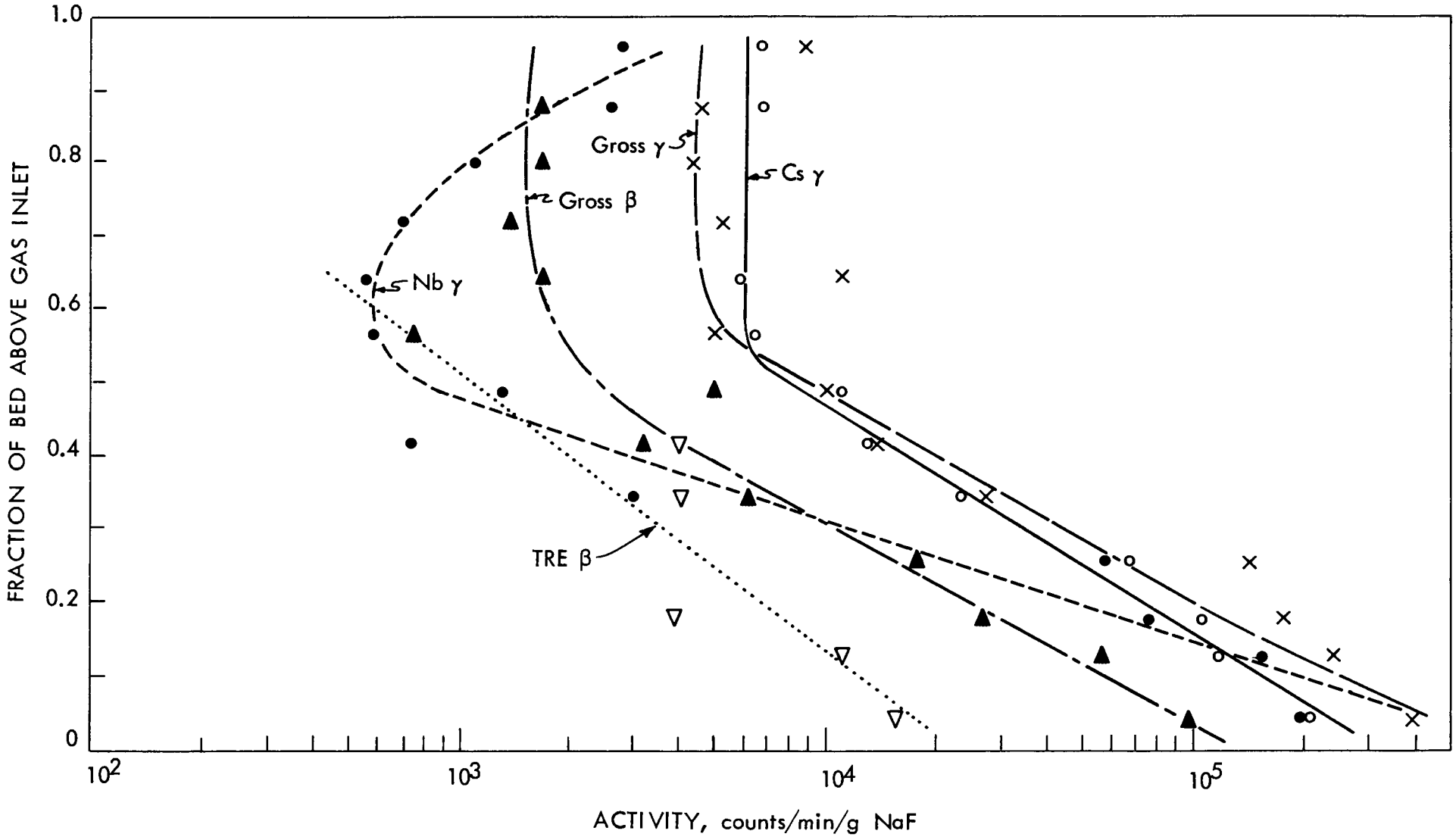

Fig. 6.2. Fission product distribution in first absorber bed.

reaction

$$UF_6 \cdot 3NaF \longrightarrow UF_5 \cdot xNaF + 0.5\ F_2$$

competes with the desorption reaction.[1] Endurance testing of absorber beds indicated that the desorption loss is independent of the number of runs (sorption-desorption cycles) for which a bed is used (Table 6.4). In each case the absorber bed was removed and analyzed only at the end of a series of runs. Chromium and zirconium fluorides were retained on the absorber beds but in low amounts (~5 g of chromium and ~1 g of zirconium per run) because the fluorinator gases were routed through the CRP trap prior to reaching the absorbers.

Table 6.4. Uranium Loss in Desorption

No. of Runs	Total Uranium Absorbed, g	Total F_2 (Desorption), moles	Total Heating Time (Desorption), hr	Uranium Left on Bed	
				wt, g	% of total
1	9,670	318	10	25	0.26
2	20,993	366	18	55	0.26
4	40,662	967	37	74[a]	0.18
7	53,856	1066	73	18	0.03
9	72,332	1945	83	18	0.03

[a]About 35 g attributed to an accidentally reversed flow direction during a purge operation.

The sorption (exothermic) and desorption (endothermic) reactions can be followed by the temperatures of the absorber beds (Figs. 6.3 and 6.4). The temperature rise during sorption is decreased by external cooling of the absorber in order to optimize conditions for sorption. The magnitude of the temperature increase indicates the relative quantities of sorbed UF_6.

Desorption of UF_6 is considered complete when the temperature of all regions of the bed reaches ~400°C. About 420°C was arbitrarily established as the maximum temperature for any part of the bed in order to minimize revolatilization of fission product fluorides and the possibility of mechanical problems, e. g., flow restriction resulting from sintered pellets. A desorption cycle generally required 9-11 hr. A period of maximum desorption rate is indicated by a temperature plateau at 310-330°C (Fig. 6.4).

Experimental studies in the pilot plant included several tests aimed at optimization of absorber operation. Absorber beds were initially composed of 12-20 mesh sodium fluoride. Because of excessive entrainment of sodium fluoride during fluorination, desorption, and various purging opera-

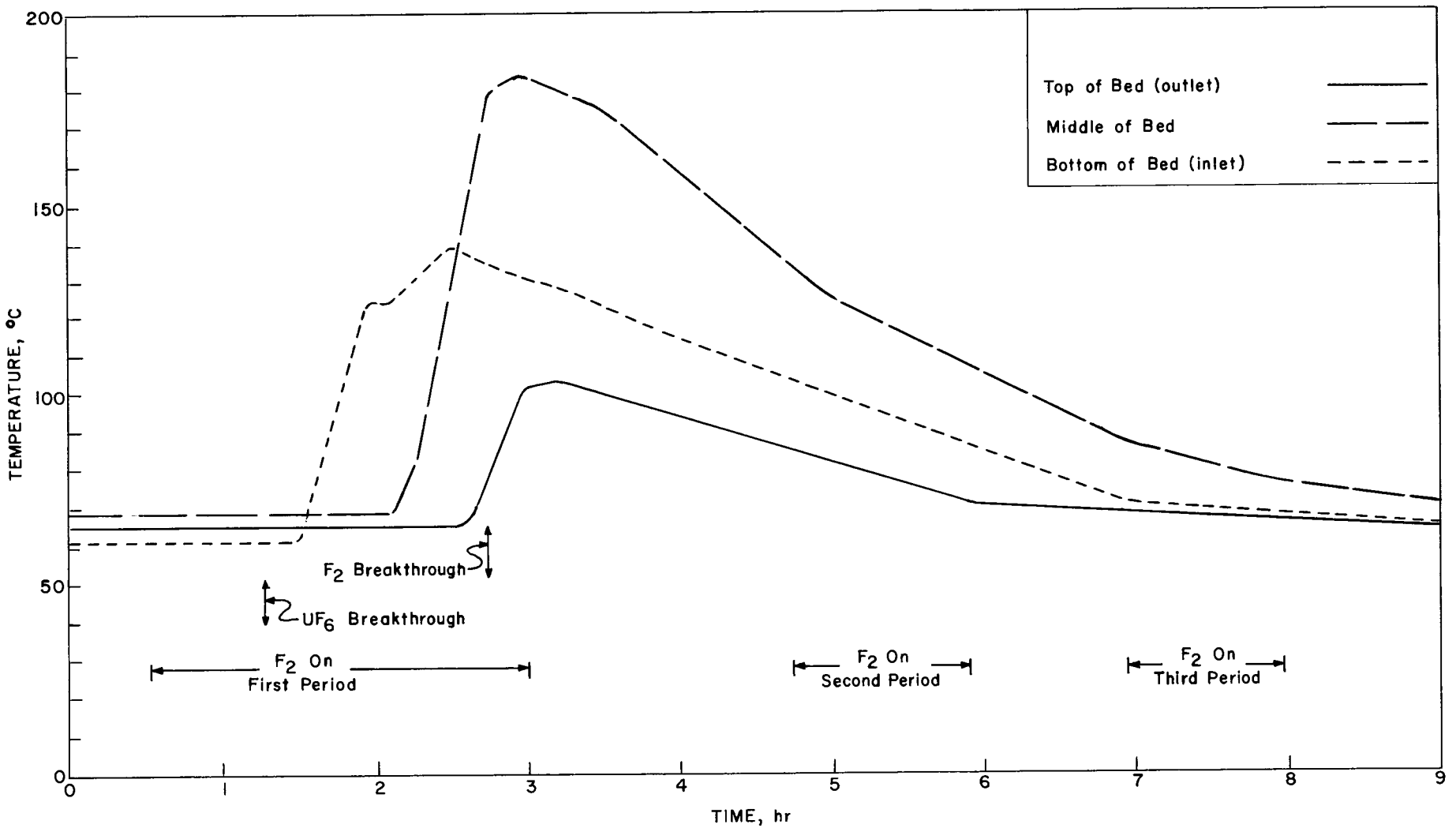

Fig. 6.3. Temperatures in absorber bed during absorption of UF_6.

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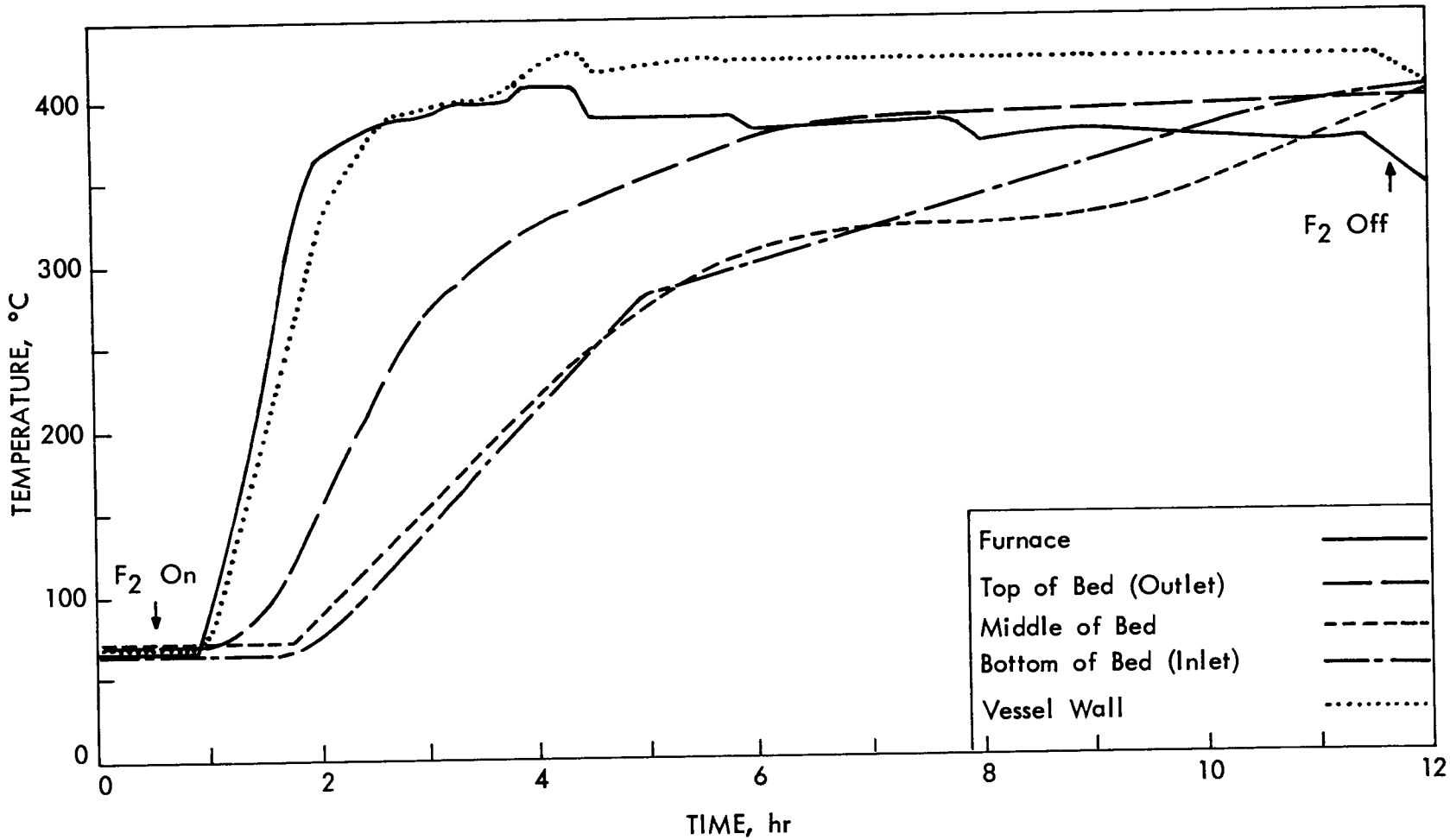

Fig. 6.4. Temperatures in first absorber during desorption of UF_6.

tions, the granulated material was replaced by 1/8-in. pellets. An expected decrease in UF_6 sorption efficiency did not materialize, so the use of pellets was adopted as standard procedure.

For economic reasons, the use of sodium bifluoride pellets was investigated. Although beds of bifluoride pellets were used successfully, the possibility of the occurrence of problems related to conversion in situ to sodium fluoride, e. g., sintering of pellets, bed shrinkage, and formation of low-melting HF-NaF complexes, outweighed the financial advantage.

6.3 Complexible Radioactive Products (CRP) Trap

This trap, a fixed bed of 1/8-in. sodium fluoride pellets maintained at 400°C, was installed in order to remove ZrF_4 "snow," entrained salt, and chromium fluorides from the gas stream leaving the fluorinator during fluorination. Certain other fission product fluorides, notably NbF_5, are also retained by the bed.

Of the materials in the melt only zirconium and chromium fluorides were present in sufficient quantity, and had sufficiently high vapor pressures, to cause equipment problems (Table 6.5). Deposition of ZrF_4 "snow" could build up in the lines and block the flow of fluorine and UF_6. During flowsheet demonstration runs valve operation was inhibited by deposition of chromium fluoride on the valve seats. Initially, a nickel mesh "snow" trap was used in the Volatility Pilot Plant, but subsequent difficulty with chromium fluoride led to the present design of a CRP trap. The feasibility of this design is being evaluated.

Table 6.5. Vapor Pressure of ZrF_4 and CrF_5

Temperature, °C	Vapor Pressure, mm Hg	
	ZrF_4[12]	CrF_5
600	0.17	>760[a]
616	0.31	a
652	1.05	a

[a]Boiling point of CrF_5 is ~110°C.

Retention of UF_6 was minimized by maintaining a bed temperature of ~400°C. Although less than 15 g of uranium was retained in a typical run (Table 6.6), beds that had to be removed during a run contained up to 194 g. Chromium retention represented 25-40% of the amount volatilized from the salt. Data on zirconium tetrafluoride retention were somewhat scattered, but in most cases <10 g of zirconium per run was deposited in the CRP trap. Distribution of uranium, chromium, and zirconium in the bed is shown in Fig. 6.5.

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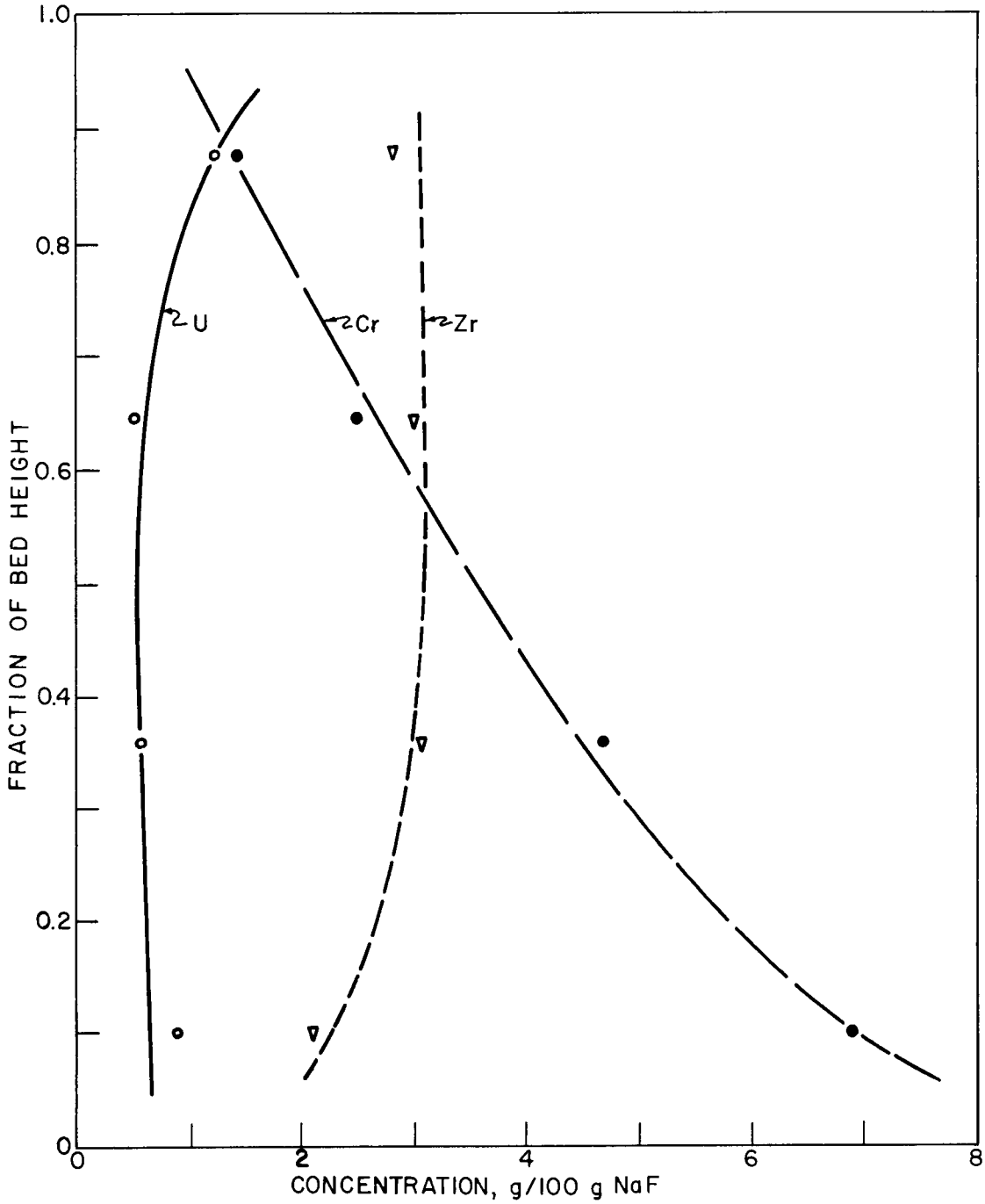

Fig. 6.5. Concentration profile of principal materials retained in CRP trap.

Table 6.6. Retention of Uranium, Chromium, and Zirconium in CRP Trap

	Uranium		Chromium		Zirconium	
Typical Run	wt, g	% of total volatilized	wt, g	% of total volatilized	wt, g	% of total volatilized
ARE	12	0.1	15	25	10	-
Development series[a]	2	0.02	13	40	8	-

[a]Bed was used in two runs before being changed.

Although basically designed for removal of zirconium and chromium fluorides, an added feature of the CRP trap was retention of fission product fluorides (Table 6.7). Niobium-95 was the only fission product present in significant quantity which formed a volatile fluoride. During the spiked run in the development series, ~97% of the volatilized NbF_5 was retained by the CRP trap. The presence of the other fission products on the bed may be attributed at least partially to entrainment (Fig. 6.6).

Table 6.7. Retention of Fission Products in the CRP Trap

	Fission Product Activity, counts/min						
Run	Gr γ	Cs γ	Nb γ	Zr γ	Ru γ	Gr β	TRE β
ARE (typical)	6.9×10^8	4.6×10^8	1.0×10^8	$<2\times10^7$	$<1.2\times10^7$	2.3×10^8	3.5×10^7
Spiked	3.3×10^{10}	2.5×10^{10}	2.3×10^{10}	5.2×10^8	6.0×10^7	1.5×10^9	3.0×10^7

The sodium fluoride bed in the CRP trap was plugged frequently during the early stages of development. However, improved heating facilities and operating techniques substantially decreased this problem. The bed had a tendency to become plugged immediately after UF_6 started to volatilize from the fluorinator. Occasionally, increased heat and/or pressure would relieve the plug, but in general the trap had to be emptied and refilled with fresh sodium fluoride pellets. Since there was no valve between the CRP trap and the fluorinator, this involved freezing the salt and purging the trap to minimize both the loss of UF_6 and any alpha contamination of the air. To date the service life of a bed has been limited by plug formation. Visual observation indicated that chromium fluoride loading is about 50% of capacity after two runs.

6.4 Plutonium

Plutonium production in uranium fuels is directly dependent on the extent of burnup and uranium enrichment. A study of plutonium behavior in the

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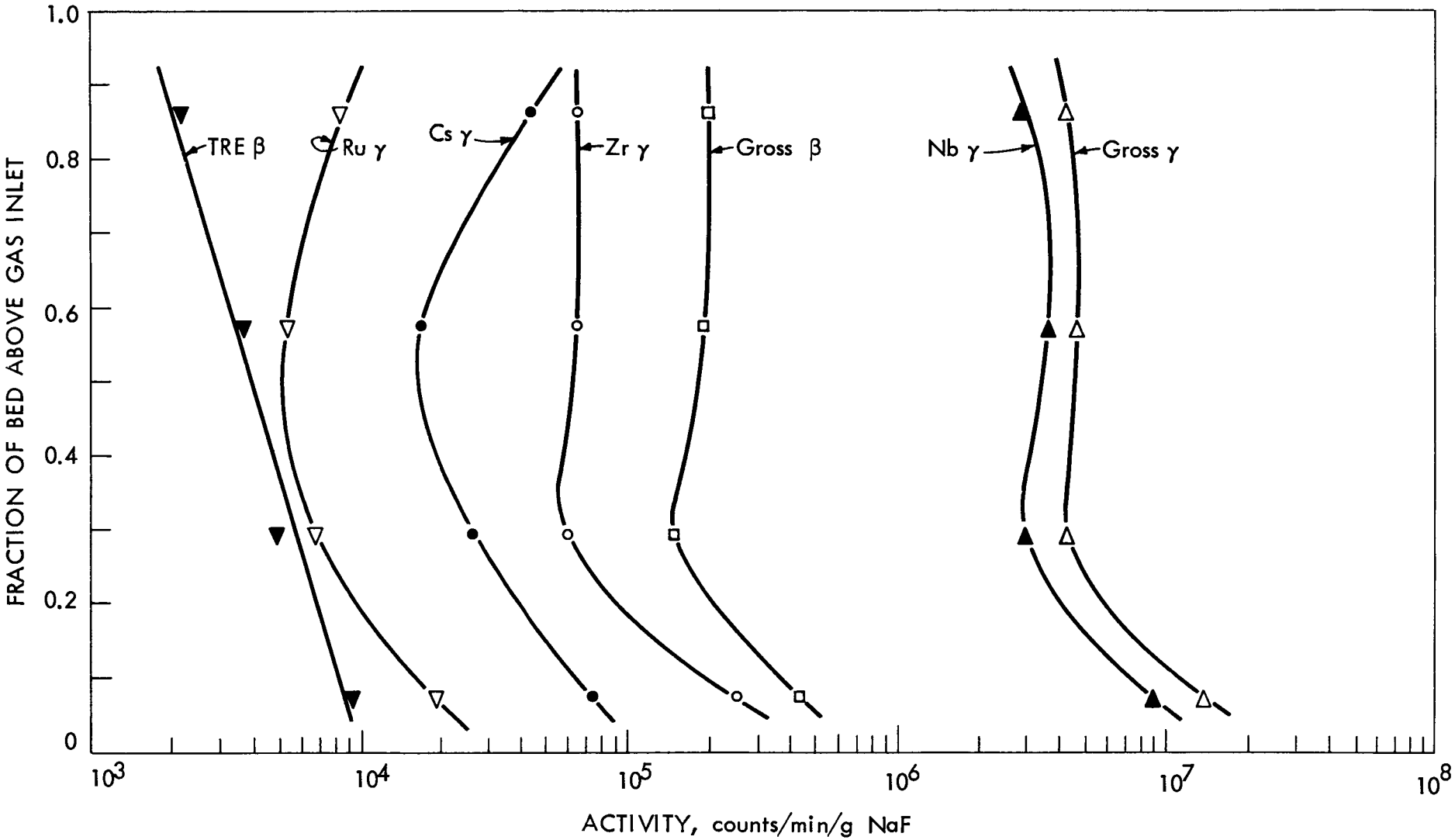

Fig. 6.6. Distribution of fission product activity in CRP trap.

Volatility Pilot Plant was considered desirable prior to processing high burnup fuels. In general, the chief consideration is contamination of the UF_6 product since the low quantities of plutonium involved diminish the significance of recovery. Fluorine reacts with PuF_4 to form volatile PuF_6. However, the reaction rate is an order of magnitude less than the analogous reaction between UF_4 and F_2, and PuF_6 is unstable except in a highly oxidizing atmosphere.[13,14]

To study plutonium behavior, PuF_4 was added to the salt charge prior to the fluorination step in the run procedure. The initial addition was limited to 10 mg of plutonium so that even if the entire amount remained with the UF_6 during processing, product contamination would be only ~1 ppm. In subsequent runs the plutonium addition was increased by factors of 10^2 and 10^3. However, each addition was dependent on favorable results from the preceding run.

During the last run (~10 g of plutonium), the fluorination period was extended 1 hr (39 moles of fluorine) after the uranium concentration was decreased to <10 ppm in a specific attempt to volatilize the plutonium. Less than 1% of the plutonium was volatilized from the molten salt (Table 6.8). About 70% of the volatilized plutonium was retained in the CRP trap

Table 6.8. Disposition of Plutonium in Process Equipment

Run	Pu Addition, mg	Volatilized from Fluorination,[a] % of initial Pu	Weight of Pu, mg			
			CRP Trap	1st Absorber	Transfer Line[b]	Product
A	10.7	0.9	0.09	-	-	<0.005
B	1.0×10^3	0.1	0.9	-	-	0.005
C	9.9×10^3	0.7	52	16	5	0.034

[a]Based on total plutonium found downstream from the fluorinator.

[b]Aqueous wash of main process line from CRP trap to absorber.

and <1 mg reached the product receiver. Maximum product contamination was 3.4 ppb, which represents a decontamination factor for plutonium of 3×10^5 (Table 6.9).

6.5 Uranium Recovery from Sodium Fluoride

One of the problems associated with the Volatility process is the handling of sodium fluoride beds. Two absorbers, one CRP trap, and three chemical traps retain uranium (on sodium fluoride beds) which cannot be recovered in situ. The quantities of uranium involved are listed in Table 6.10.

Table 6.9. Decontamination Factors for Plutonium

Run	Plutonium, α cpm/mg U		Over-all D. F.
	Feed Salt	Product	
A	46	$<4\times10^{-2}$	$>1.2\times10^{3}$
B	1.1×10^{4}	4×10^{-2}	2.5×10^{5}
C	8.5×10^{4}	0.28	3.0×10^{5}

Table 6.10. Uranium Retention on Sodium Fluoride Beds

Vessel	NaF, kg	Uranium, g per typical run	Estimated Service Life of Bed, runs	Comments
CRP trap (FV-103)	7	2-5	~2	Up to 300 g uranium retained when bed plugged; service life limited by plugs and CrF_5 sorption
1st absorber (FV-120)	26	2-7	>9	Uranium retention per run is dependent on frequency of bed changing
2nd absorber (FV-121)	26	1-4	>9	
Chemical trap in vacuum line (FV-122)	3	~3	~250	
Chemical trap in main process line (FV-124)	11	10-15	~500	Up to 300 g uranium retained when cold traps are purged
Chemical trap in heated duct system (FV-158)	7	<1	>500	
Total	80	19-35		

The total retention during a typical run represents 0.2 to 0.4% of the feed. Uranium tended to accumulate in the three chemical traps whereas retention in the absorbers and CRP trap seemed to be independent of the quantity of uranium processed through the bed. However, the service life of a chemical trap, estimated from its capacity for uranium to be 250-500 runs, was restricted to three or four runs by the necessity for uranium accountability. Also, mechanical difficulties, such as plugging, necessitated unscheduled bed changes. To date, radioactivity in the system has not been high enough to affect the methods used in handling these beds, but if short-decayed fuels

are processed in the present system, the absorbers and CRP trap will retain considerable fission product activity.

Primarily because of convenience resulting from available aqueous processing facilities, the present system for recovering uranium from sodium fluoride beds involves (a) removal of the bed from its vessel and (b) dissolution of the pellets in 0.1 M HNO_3, followed by (c) uranium recovery in an aqueous processing facility (solvent extraction and precipitation). The main drawback to the above method was the large volumes of dilute solutions which had to be handled. Sodium fluoride solubility in the acid solution was 1 to 2 wt %. Two schemes to concentrate the solutions were proposed: (1) reduction of UO_2F_2 to UF_4 with iron filings followed by dissolution of the precipitate (UF_4) in a 2 M $Al(NO_3)_3$—2 M HNO_3 solution to which was added 14 g of $Fe(NO_3)_3 \cdot 9H_2O$ per 100 ml; and (2) sorption on Dowex-1 anion exchange resin in an ion exchange column followed by elution with 6 M HNO_3. However, neither concentration technique was developed to the point of successful operation. Also, it should be noted that these methods were applicable only to low-activity materials.

No acceptable method of recovering uranium from sodium fluoride beds containing highly radioactive materials has been proposed. Instead, effort will be directed toward minimizing uranium retention in these areas, i. e., CRP trap and the two absorbers.

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8.0 REFERENCES

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

2. A. M. Weinberg et al., "Nuclear Science and Engineering," Vol. 2, pp. 797-853 (supplement to November 1957 issue). Same as "Molten Fluoride Reactors," ORNL-CF-57-6-69.

3. W. H. Carr, "Volatility Processing of the ARE Fuel," Chemical Engineering Progress Symposium Series, Nuclear Engineering, Vol. 56, Book No. 28, Part 8, (1960).

4. R. P. Milford, "Industrial and Engineering Chemistry," Vol. 50, No. 2, pp. 187-191, February 1958.

5. J. B. Ruch, "Volatility Pilot Plant - Waste Transfer Studies," ORNL-CF-58-5-62, May 21, 1958.

6. J. T. Long, "Industrial and Engineering Chemistry," Vol. 51, pp. 169-173, February 1959.

7. F. W. Miles, "Engineering Evaluation of Volatility Pilot Plant Equipment" (to be published as an ORNL-CF memo).

8. A. P. Litman and A. E. Goldman, "Corrosion Associated with Fluorination in the Fluoride Volatility Process," ORNL-2832 (in press).

9. "Memo #38, Inspection of Volatility Pilot Plant Process Vessels," A. P. Litman, ORNL Metallurgy Division, to W. H. Carr, November 18, 1958.

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

11. W. A. Brooksbank, Jr., R. J. Carter, M. F. Osborne, "Volatility Studies of Some Fission Product Fluorides," ORNL-CF-58-6-86, June 25, 1958.

12. Karl A. Sense et al., "Vapor Pressures of the Sodium Fluoride-Zirconium Fluoride System and Derived Information," BMI-1064, January 9, 1956.

13. I. R. Tannebaum, and A. E. Florin, "An Improved Apparatus for the Preparation of Plutonium Hexafluoride," LA-1580, May 15, 1953.

14. "Argonne National Laboratory Chemical Engineering Division Summary Report - October, November, and December, 1956," ANL-4668.

15. "ORNL Master Analytical Manual," ORNL-CF-53-1-235.

9.0 APPENDIX

9.1 Sampling

Several sampling methods had to be developed to evaluate pilot plant operation. These techniques are described in more detail in reference 7.

Molten Salt. Molten salt in the fluorinator was sampled before and after a period of fluorination to determine the extent of the reaction and for uranium accountability. If additional fluorination was necessary, salt samples were taken at regular intervals until the uranium concentration was decreased to a waste salt level. Generally, four or five samples were taken each time, the individual samples containing ~2 g of salt.

Fig. 9.1. Copper sample ladle used for molten salt sampling.

Prior to sampling the melt was sparged with nitrogen at a rate of 20 standard liters/min for 3/4 hour to homogenize the mixture. Sample ladles, 3/8-in. copper tubes closed at both ends and notched in the middle, suspended from a wire and reel arrangement, were lowered into the fluorinator through a purged sample line (Fig. 9.1). A power-driven reel then raised the ladle (filled with salt) to a pedestal where subsequent handling was dependent on the radioactivity of the salt. Salt was removed from sample ladles by hammering the ladles until the contained salt was pulverized. The resulting powder could then be poured into a sample bottle. During operation the entire assembly was housed in a Lucite hood and maintained under a positive nitrogen pressure.

Uranium Hexafluoride Product. Product was sampled prior to shipment to determine its chemical purity and radioactivity, and for uranium accountability. Four or five samples were taken, each containing ~6 g of UF_6, from each product cylinder.

A Fluorothene sample tube was connected through a sampling manifold to a product cylinder at ~100°C. The manifold was filled with UF_6 liquid, and then cooled. The UF_6 was then drained into a sample tube.

Sodium Fluoride Beds. Vessels containing sodium fluoride beds (traps, absorbers) were sampled in order to evaluate performance and to recover contained uranium. Sampled, as used here, is somewhat of a misnomer since the entire bed was removed in each case. The frequency of sampling was varied to obtain specific information from a run.

Generally, the pellets were removed from the vessel in layers of ~2 kg each. Each layer was dissolved independently in 0.1 M HNO_3. Dissolution was performed in a heated drum (~60°C), and the final solution contained ~1 wt % NaF. A pH of 1 was maintained to prevent uranium from being reduced to uranium(IV) and precipitating. The drums were lined with polyethylene to prevent uranium from being reduced by the iron. Two or three sets of 15-ml duplicate samples were taken from each drum of solution. The remaining solution was subsequently processed for uranium recovery or discarded, depending on the economics for recovery by aqueous methods.

9.2 Analytical Methods

Samples were analyzed by chemical, radiochemical, spectrographic, and isotopic procedures. In general, standard methods of analysis were used.

Precise uranium determinations were required in order to evaluate the process and for accountability purposes. A summary of the methods for uranium determination is given in Table 9.1. Detailed procedures are given in the ORNL Master Analytical Manual.[15]

Table 9.1. Uranium Determination in Volatility Pilot Plant Samples

Sample	Method of Analysis	Precision, %	Comments
UF_6 product	Potentiometric ferric sulfate	± 0.2	
Feed salt	Potentiometric ferric sulfate	± 0.5	Necessity of pretreatment to remove interfering ions causes the relatively poor precision
Waste salt	Fluorimetric	±10	More accurate method was unnecessary because of small quantity of uranium present
NaF dissolutions	Fluorimetric or spectrophotometric ammonium thiocyanate	±10	Method used is dependent on uranium concentration; fluorimetric for samples < 0.1 mg/ml

No standard procedure was available for the determination of plutonium in UF_6 samples. A procedure was developed which involved LaF_3 precipitation and TTA (trithenoyl acetone) extraction, followed by determination of the α count rate. Results from analysis of known samples indicated the analytical error to be about ±15% in the parts per billion range.

The chief impurities in the feed salt and the UF_6 product were determined both chemically and spectrographically.

9.3 Leak Testing

After a major loss of UF_6 from the system during the ARE program indicated the necessity for a gastight system, all service piping was modified to eliminate as many joints and fittings as possible. A three-phase program for leak elimination was then undertaken.

Initially the system was pressurized with nitrogen; any leaks detectable with soap bubbles were eliminated. The second phase involved pressurizing the system with Freon and then using a halide leak detector to detect leaks that were too small to be detected with soap bubbles. After these leaks were repaired, the third phase served to eliminate leaks too minute to be detected with Freon. All fittings and joints were identified and numbered. The system was then pressurized with fluorine. Each joint was wrapped with absorbent paper, e. g., Kleenex, which was then soaked with potassium iodide—starch solution. Any leakage of fluorine would discolor the paper and, if the leaks were small enough, would pinpoint its exact location. Every joint in the system was proved leaktight to this test before operations were resumed. Throughout subsequent operations, records of all fittings were maintained, and any joint that was disturbed (e. g., for maintenance) was again leak-tested with fluorine before being put back into service.

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