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Uranium - Zirconium Alloy Fuel Processing in the ORNL Volatility Pilot Plant - Paper for Presentation at the AIChE Symposium, "Volatility Reprocessing of Nuclear Reactor Fuels," New York, New York, December 1961

W. H. Carr, S. Mann and E. C. Moncrief

ABSTRACT

The Volatility Pilot Plant is currently engaged in a development program on zirconium-uranium alloy fuel processing. Fourteen dissolution runs have been made at 650-500°C in a molten salt of equimolar NaF-LiF containing 25 mole % ZrF_4. Seven runs have been carried through the fluorination phase at 500°C with the UF_6 product being sorbed on and desorbed from NaF and collected in a cold trap. Over-all fuel dissolution rates of 3.68 kg/hr were obtained with HF utilizations of 30-45%. Uranium losses per run were <0.31% of the uranium feed. Chemical contaminants in the uranium product were primarily sodium, molybdenum, and copper. The principal process operating difficulty has been off-gas valve plugging due to submicron size particles generated during the dissolution reaction.

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INTRODUCTION

A Fluoride Volatility Process for recovery of nuclear fuels has been developed by Oak Ridge National Laboratory.[1,2] The distinguishing features of the ORNL process are fluorination with elemental fluorine in molten salt to produce uranium hexafluoride and further purification by an absorption-desorption cycle in a bed of sodium fluoride pellets. Development of the process has been carried into the pilot plant stage.

The Volatility Pilot Plant at Oak Ridge National Laboratory was originally constructed for the recovery of the Aircraft Reactor Experiment fuel. This fuel was a mixture of sodium, zirconium, and uranium fluorides with a melting point slightly above 600°C and containing 62 kg of fully enriched uranium. The burn-up was very low, so that the activity level was only 10^5 γ counts per minute per milligram of uranium. This material was recovered with a uranium loss of 0.7% and decontaminated to the activity level of unirradiated uranium. An inadvertent UF_6 leak accounted for 90% of this uranium loss.

Following recovery of the ARE fuel, a similar reactor charge containing 72 kg of uranium was processed. Since this second fuel charge was essentially nonirradiated, three of the runs were spiked with irradiated loop material. The spike brought the gross activity level only up to that of the ARE fuel, but since the loop material was short-decayed, the fission-product spectrum was different. Again, decontamination was complete within the limits of detection; the activity of the UF_6 product was that of unirradiated uranium. For this second reactor fuel, uranium recovery was measured as 100.4%. Measured losses were 9 g, or 0.012%.[3]

PROCESS

The ORNL Volatility Pilot Plant has recently been modified for processing zirconium-uranium alloy fuels.[4] In HF dissolution, fuel elements are lowered into the dissolver (Fig. 1) and covered with barren salt consisting of equimolar NaF-LiF and containing 25 mole % ZrF_4. Anhydrous HF from the circulating system is bubbled up through the salt and fuel elements, converting the zirconium and uranium to the tetrafluorides, both of which are soluble in the salt. Off-gas from the dissolution (hydrogen plus unreacted HF) can be routed either directly to a KOH neutralizer or into the recirculation system. This recirculation system consists of a refrigerated-water cooler, a Freon-cooled condenser vented through the KOH solution, an accumulator, a diaphragm

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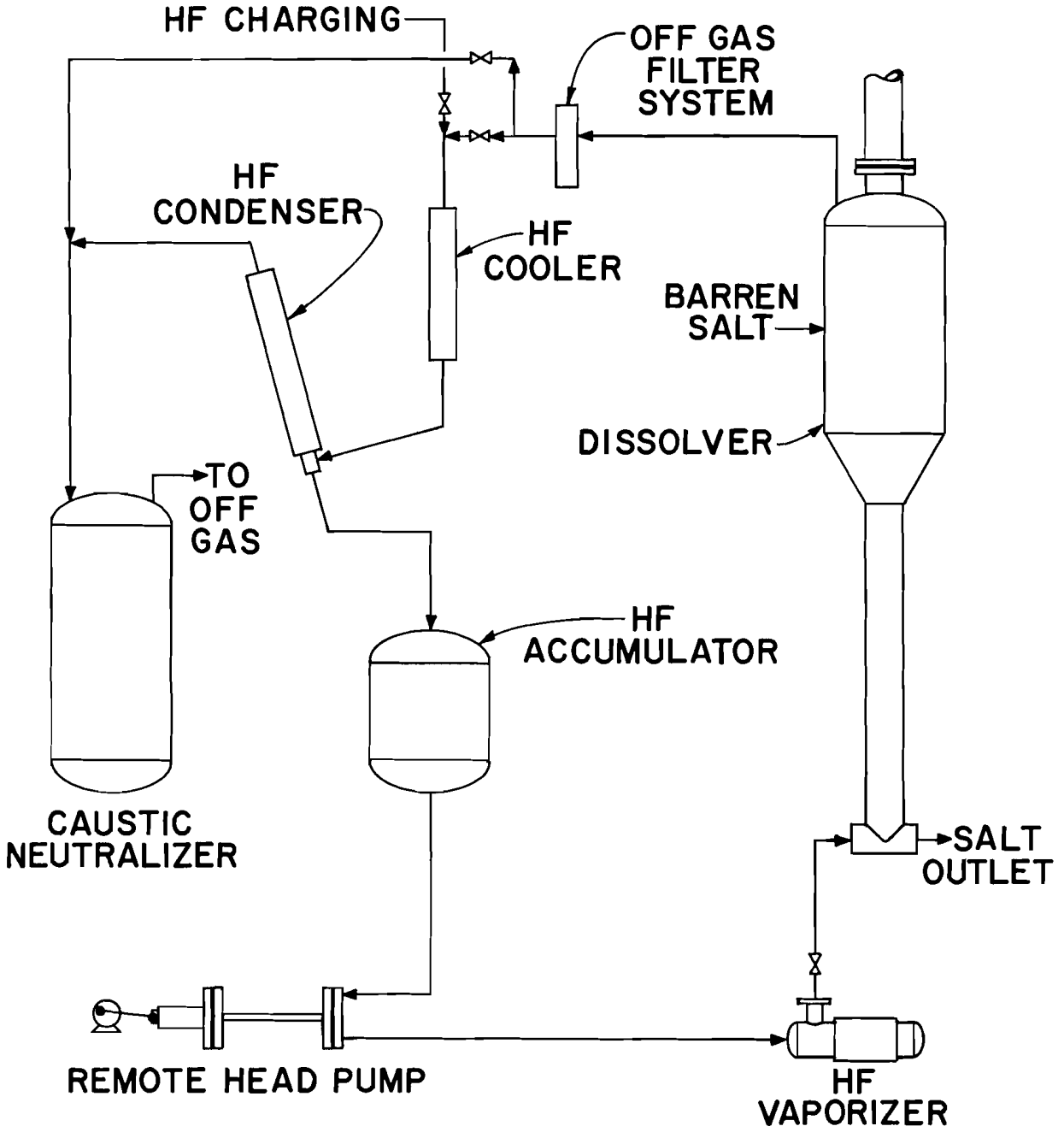


VOLATILITY PILOT PLANT
DISSOLUTION FLOW SHEET

FIG. 1

pump, and a steam-jacketed vaporizer. Details of the off-gas solids filter system will be discussed later.

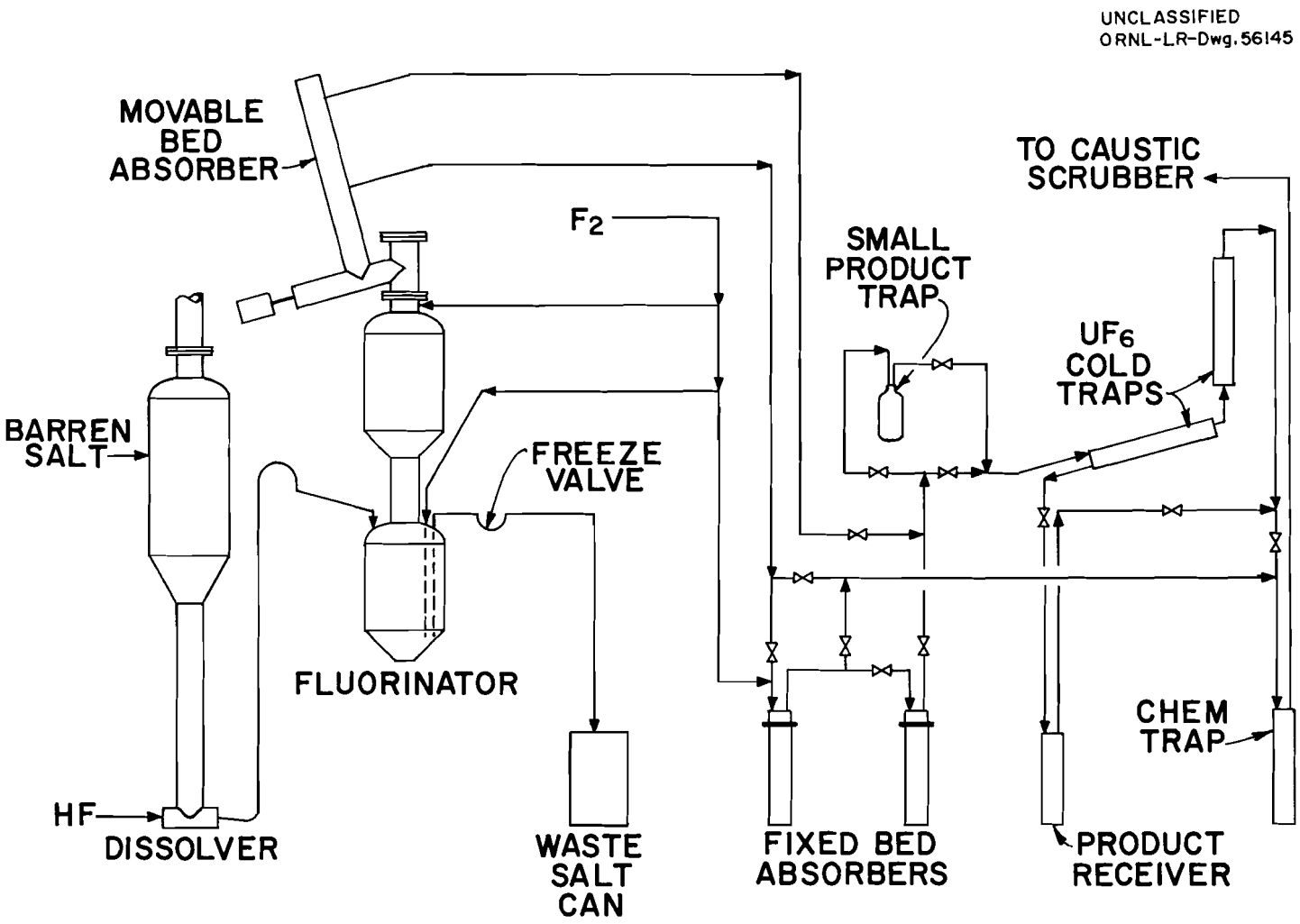
Figure 2 shows the flowsheet for the entire uranium system. After dissolution is complete, the salt containing the UF_4 is transferred to the fluorinator, where it is contacted by elemental fluorine which converts the UF_4 to volatile UF_6. After fluorination is completed, the waste salt, containing 99.9% of the fission products, is transferred to a shielded waste salt can for disposal in the burial ground.

During fluorination the UF_6, excess fluorine, and other gases are routed through a sodium fluoride bed at about 100°C. The plant is built for use of either fixed-bed absorbers or a movable-bed absorber which will be described later. Assume for the moment that the movable-bed absorber is serving only as piping leading to the two fixed-bed absorbers. The sodium fluoride pellets in the first fixed-bed absorber, held between 65 and 125°C, will absorb the UF_6 and most of the fission products from the gas stream. The excess fluorine and inert gases next pass in sequence through the second sodium fluoride bed at ambient temperature to prevent possible loss of UF_6 and a KOH scrubber system for removal of fluorine, and are then exhausted to the off-gas stack.

After fluorination and absorption are complete, valving is changed to provide a flow of fluorine through the two fixed bed absorbers in series. Both absorbers are heated to 400°C, releasing the UF_6 but retaining most of the fission products on the sodium fluoride beds. The gas stream containing the UF_6 goes through the cold traps to freeze out the UF_6 and then through the chemical trap (for trace UF_6 removal) to the off-gas system.

The two cold traps and the product receiver were initially installed for handling 10-kg batches of uranium. Since in current runs ~ 0.5 kg is recovered, a product cylinder sized for one run was installed so that data could be obtained for each run. Sampling of individual product cylinders is primarily for the evaluation of chemical contaminants in the product during cold runs and of chemical and radiochemical contaminants during hot runs. Upon completion of a series of runs, all the UF_6 is transferred from the small cylinders to the large cold traps and then to a standard 5-in.-ID product receiver for shipment as a single batch.

The movable bed (temperature-zoned) absorber is shown in more detail in Fig. 3. The first portion of sodium fluoride is held at 400°C in zone 1.



VOLATILITY PILOT PLANT
URANIUM SYSTEM

FIG. 2

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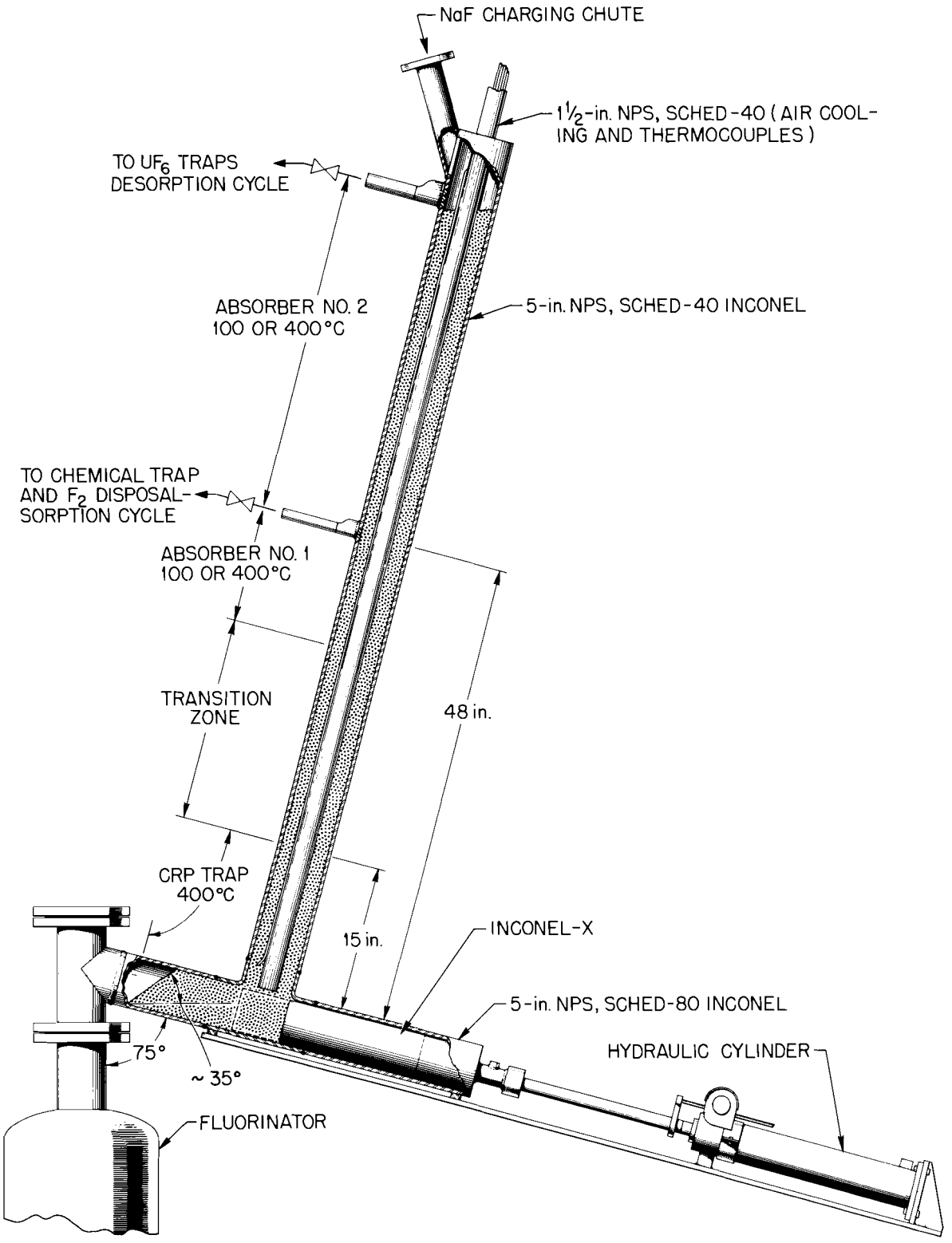

FIG. 3 MOVABLE BED TEMPERATURE-ZONED ABSORBER.

At this temperature UF_6 is not absorbed, but the fluorides of most of the fission and corrosion products in the gas stream, including zirconium, ruthenium, and chromium fluorides, are absorbed or filtered out. Thus this zone of the absorber serves as a complexible radioactive products (CRP) trap. Above the CRP trap section, the vessel is cooled from 400 to 100°C in a transition zone. Above the transition zone and below the lower outlet there is a third zone held at approximately 100°C; thus, using the lower outlet directly to the chemical trap, this portion serves the same function of the first fixed bed absorber. For desorption, valving is changed to the upper outlet and the entire vessel is heated to 400°C. The upper zone of the vessel serves as the second fixed-bed absorber, and the gas stream leaving through the upper outlet goes directly to the product collection system.

Prior to discharge of waste salt from the fluorinator, the sodium fluoride in the horizontal section of the CRP trap (zone 1) is discharged by a hydraulically operated piston into the waste salt. The sodium fluoride dissolves readily, and the radioactive material trapped by the sodium fluoride is thus disposed of with no additional waste streams.

After discharge of the sodium fluoride from the horizontal section, the piston is retracted, allowing the entire vertical bed to drop, and the horizontal bed is re-formed by repeated short strokes of the piston. Sufficient excess sodium fluoride capacity is provided in the top zone that several runs can be made before additional pellets need to be charged. Recharging the CRP trap permits an additional process simplification. Formerly, aqueous operations were required to recover uranium from chemical traps. Now, the sodium fluoride from chemical traps can be used for recharging the movable-bed absorber, with the residual UF_6 on the sodium fluoride being recovered in the next desorption.

Since the movable-bed absorber is directly connected to the fluorinator and combines all UF_6 purification and decontamination steps following fluorination, it is possible to eliminate high activity levels in valves and piping downstream from the fluorinator. If this equipment proves reliable during an extended period of hot runs, it should significantly simplify future installations.

In Fig. 1, a filter was shown in the dissolver off-gas line. This filter was not a part of the original installation since the enlarged top section of

the dissolver was expected to prevent solids entrainment. However, when the first two dissolutions were interrupted by plugging of the off-gas valves, the need for a filter or solids separator became apparent. The plugging was traced to sub-micron sized solid particles generated during the dissolution and either volatilized or entrained to the off-gas stream. These particles are 25 to 40% salt, the remainder being metallics, principally iron, tin, chromium, nickel, and molybdenum; about 300 g was evolved in each dissolution. These solids constitute the most critical operational problem in the Volatility Pilot Plant at this time. Various methods of filtration, such as porous metal filters, cyclones, and copper mesh filters, were tried, of which the copper mesh filter, providing a large amount of impingement surface, was the most successful. However, none was entirely satisfactory since some solids continued to reach the off-gas valves.

Currently, a system for continuous washing of the off-gas line with liquid HF is being installed. The revised flowsheet incorporating this washing system is shown in Fig. 4. The principal change from the original HF dissolution system is substitution of the middle portion of Fig. 4 for the off-gas filter in Fig. 1. The gas outlet from the dissolver is a short section of 2-in.-dia pipe from the charging chute to the HF flash cooler, which is a section of 6-in.-dia pipe with liquid HF pumped in the top. Sufficient liquid HF is pumped to the flash cooler to cool all the off-gas to the HF dew point and still have some liquid washing the wall. Theoretically, the off-gas solids should be removed from the gas stream primarily by impingement followed by liquid HF washing. The two packed sections shown above and below the HF condenser are removable. Initial evaluations will be made with copper mesh packing of the type used previously in the off-gas filter. It is hoped that the packing will prove to be unnecessary. Between the two packed sections is the HF condenser consisting of a length of pipe jacketed with coolant (0°C water-ethylene glycol) for condensing HF. The inlet to the 8-in.-dia catch tank is submerged. Noncondensibles flow to the reboiler at the top, the HF level being equalized through the lower line. The reboiler is a section of 8-in.-dia pipe with a steam jacket down to, but not covering, the dished head, so that boiling will not occur unless there is a liquid level of at least 2 to 3 in. in the reboiler and a foot of inlet submergence in the catch tank. During evaluation tests the vapor from the reboiler will

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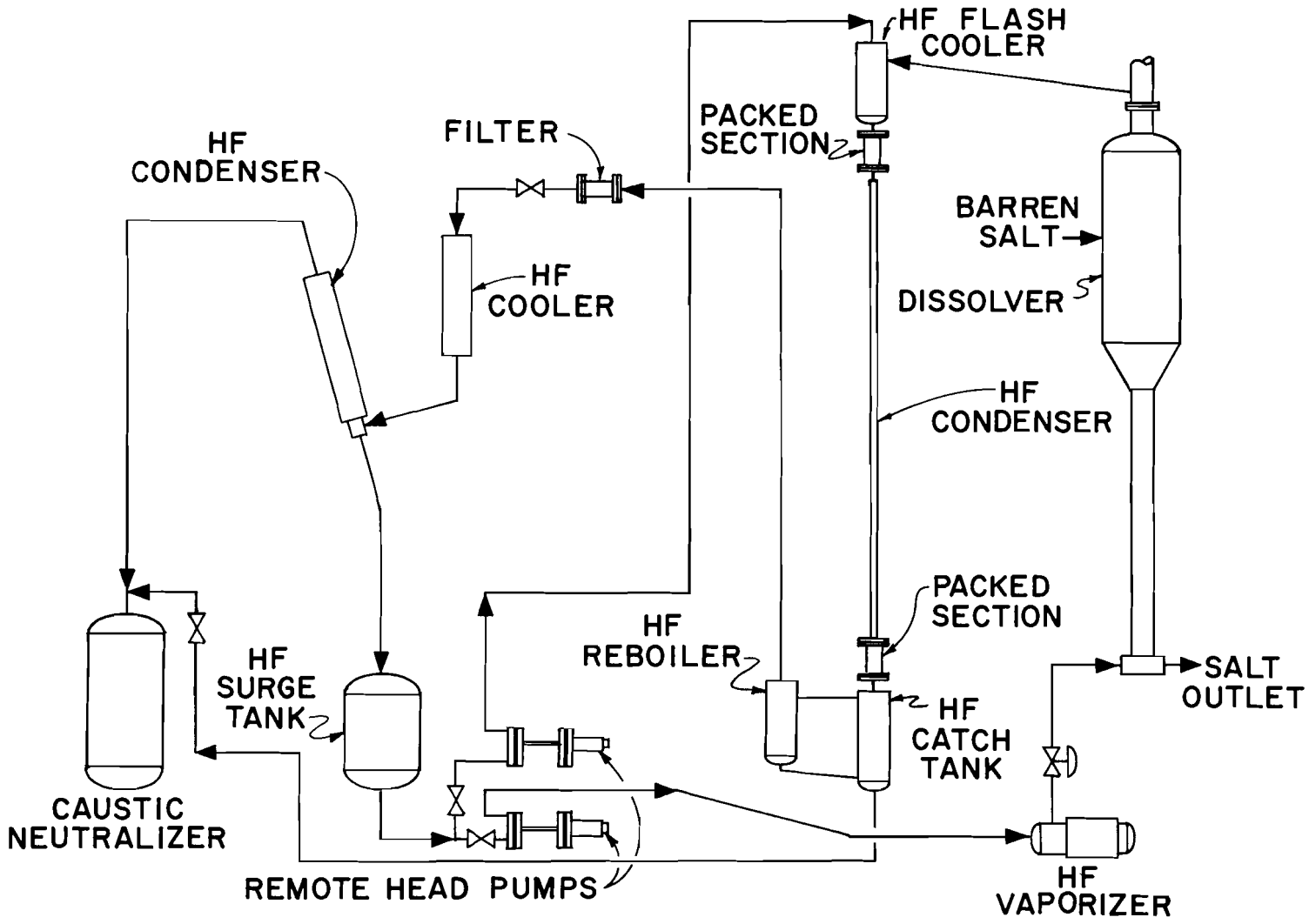

VOLATILITY PILOT PLANT HF SYSTEM

FIG. 4

go through a temporary copper mesh filter before entering the present HF recirculation system. An additional pump is included to supply liquid HF to the flash cooler. At the end of each run, the solids collected and the liquid HF remaining in the catch tank and reboiler will be discharged to the caustic neutralizer.

EQUIPMENT

Some views of the actual equipment may be of interest. Fig 5 is a drawing of the dissolver. The fuel and HF are contacted in the 5-in.-dia section at the bottom. The normal liquid level is in the cone, and the upper section allows de-entrainment. Fig 6 is a view of the dissolver in place without the charging chute during construction. Fig 7 is a view of the bottom of the dissolver with one side of the furnace open. The HF inlet line, not yet insulated, is on the left, and the salt outlet line is on the right. Heating elements are visible in the walls of the entry port. Fig 8 shows a dummy fuel element inside the dissolver just above the 5-in.-dia section. The vertical scale is quite distorted; the black circle is the 5-in.-dia bottom section; the dummy element is about 4 ft long.

Fig 9 shows the HF condensing system. The cooler on the left uses chilled water for heat transfer, and the other unit is Freon-cooled.

Fig 10 is a picture of the fluorinator. The furnace for the bottom section has been lowered; the top section had not been insulated when this picture was made, and the Calrods used for heating the upper section are viaible. Fig 11 is a diagram of the fluorinator with the furnace in operating position, showing details such as the draft tube into which the fluorine is admitted.

Fig 12 is a portion of the control panel, showing primarily the graphic panel which includes most of the pneumatic instruments and valve controls.

DATA AND RESULTS

The first work after construction was component testing. After completion of component testing with barren salt, development runs were made in which processing conditions were varied for experimental purposes. A few of the variables, e.g. fluorine flow rate, are still being studied; the principal conditions, which have been tentatively fixed, are: (a) dissolution temperature ~ 50°C above the salt melting point (in most cases, the initial temperature will be 650°C, gradually decreased to 500°C as dissolution proceeds), (b) HF

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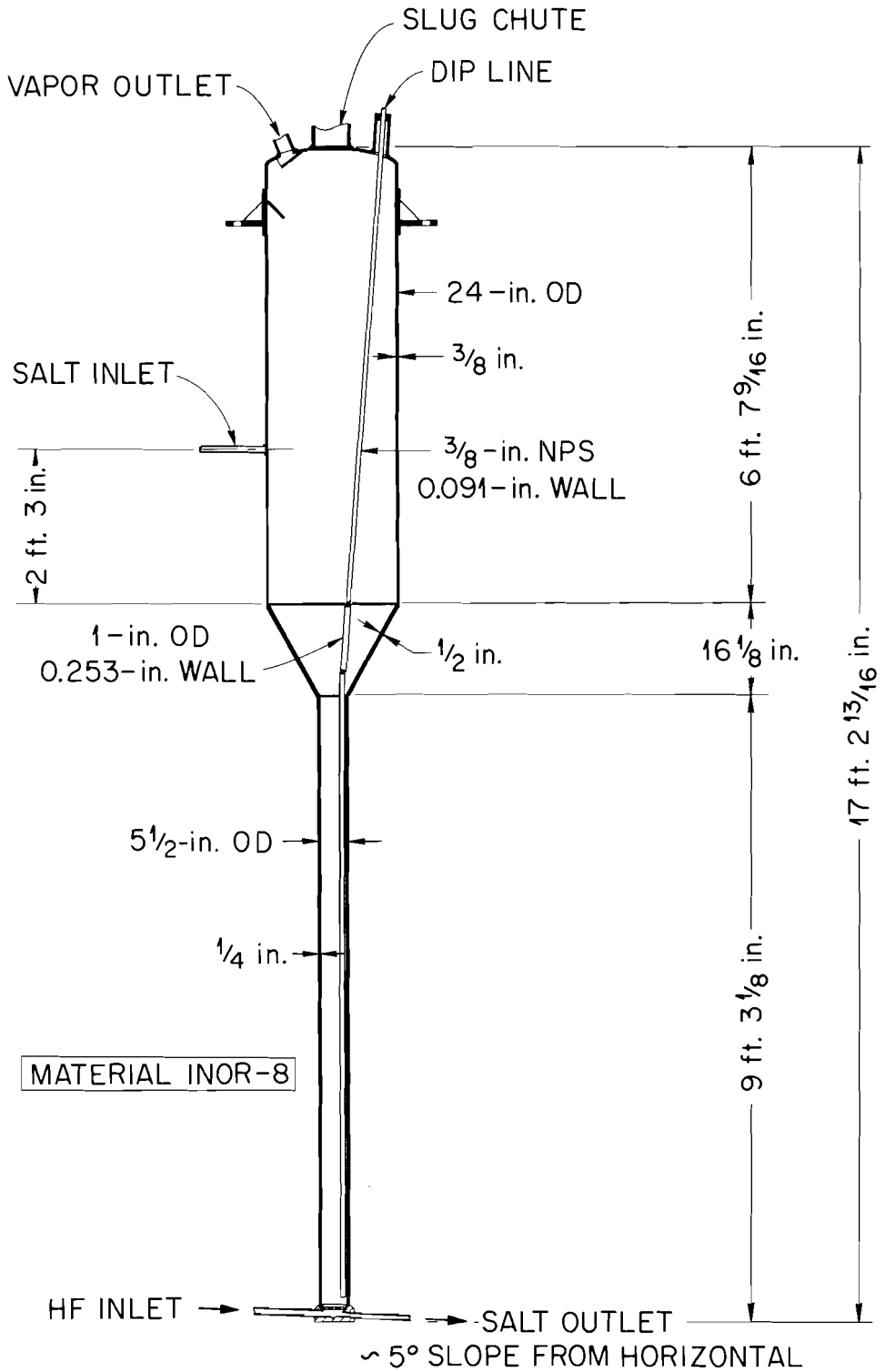

FIG. 5 DISSOLVER

FIG. 6 DISSOLVER

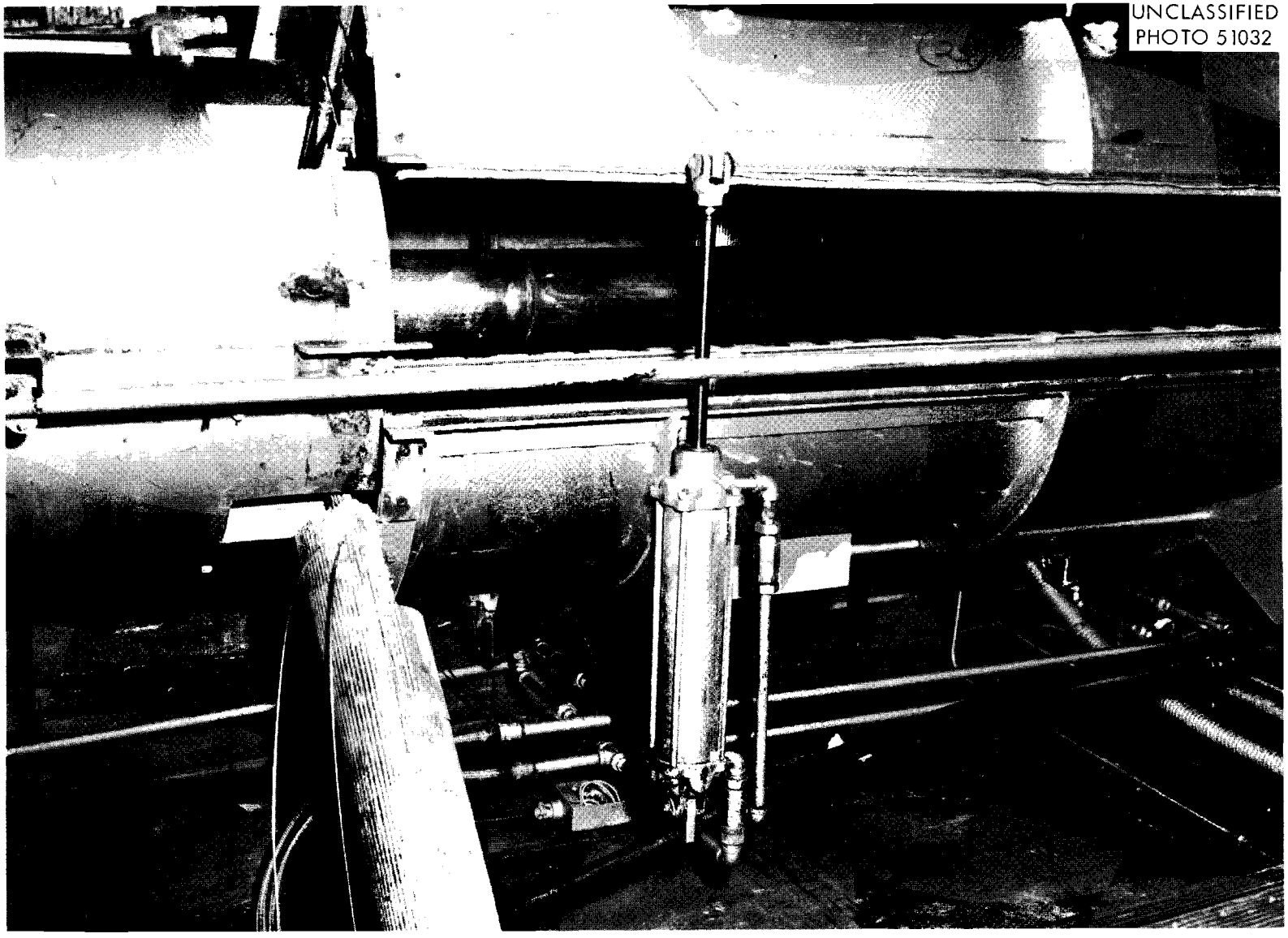

FIG. 7 DISSOLVER AND FURNANCE

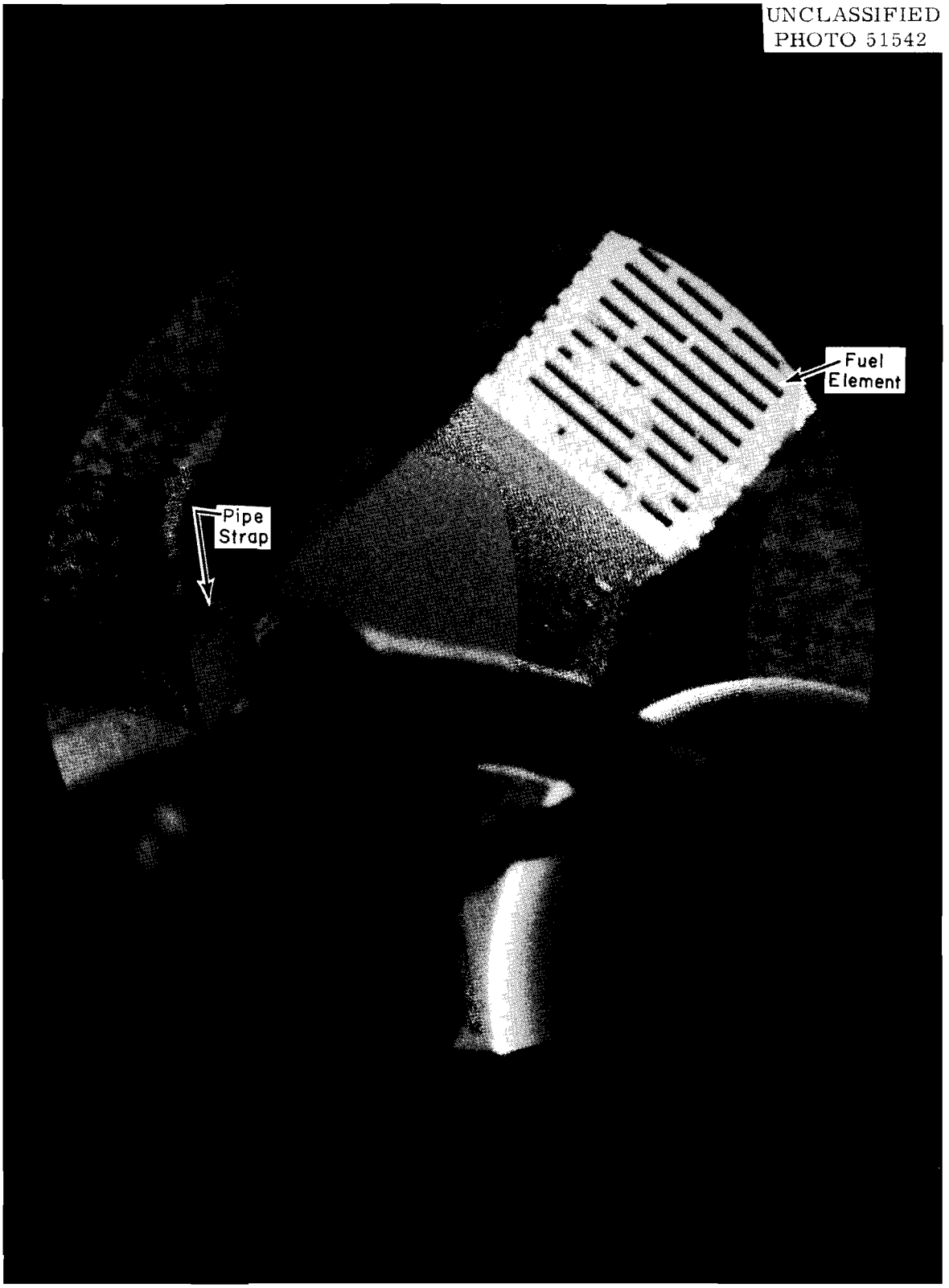

FIG. 8 DISSOLVER INTERIOR

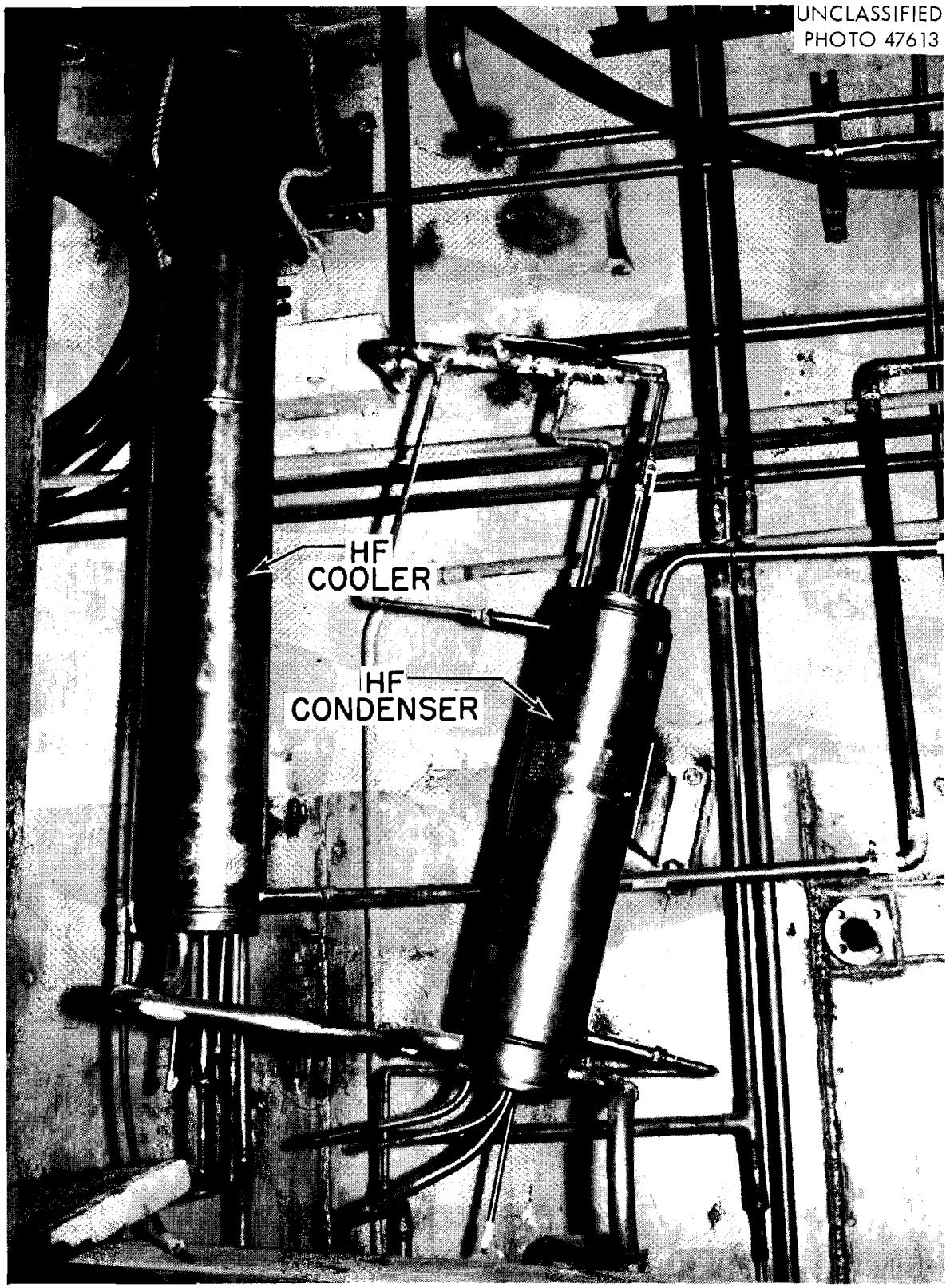

FIG. 9 HF COOLER AND CONDENSER

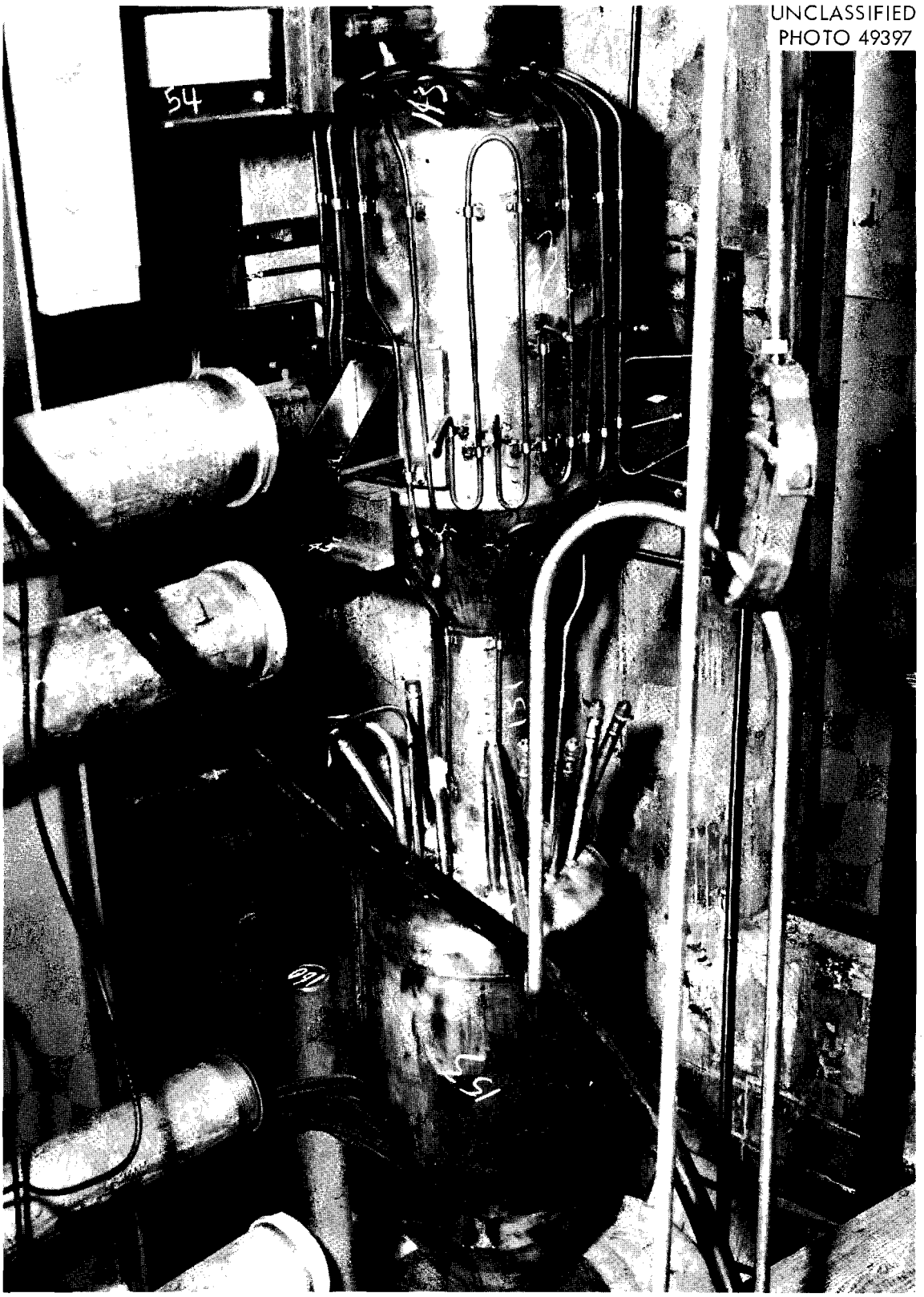

FIG. 10 FLUORINATOR

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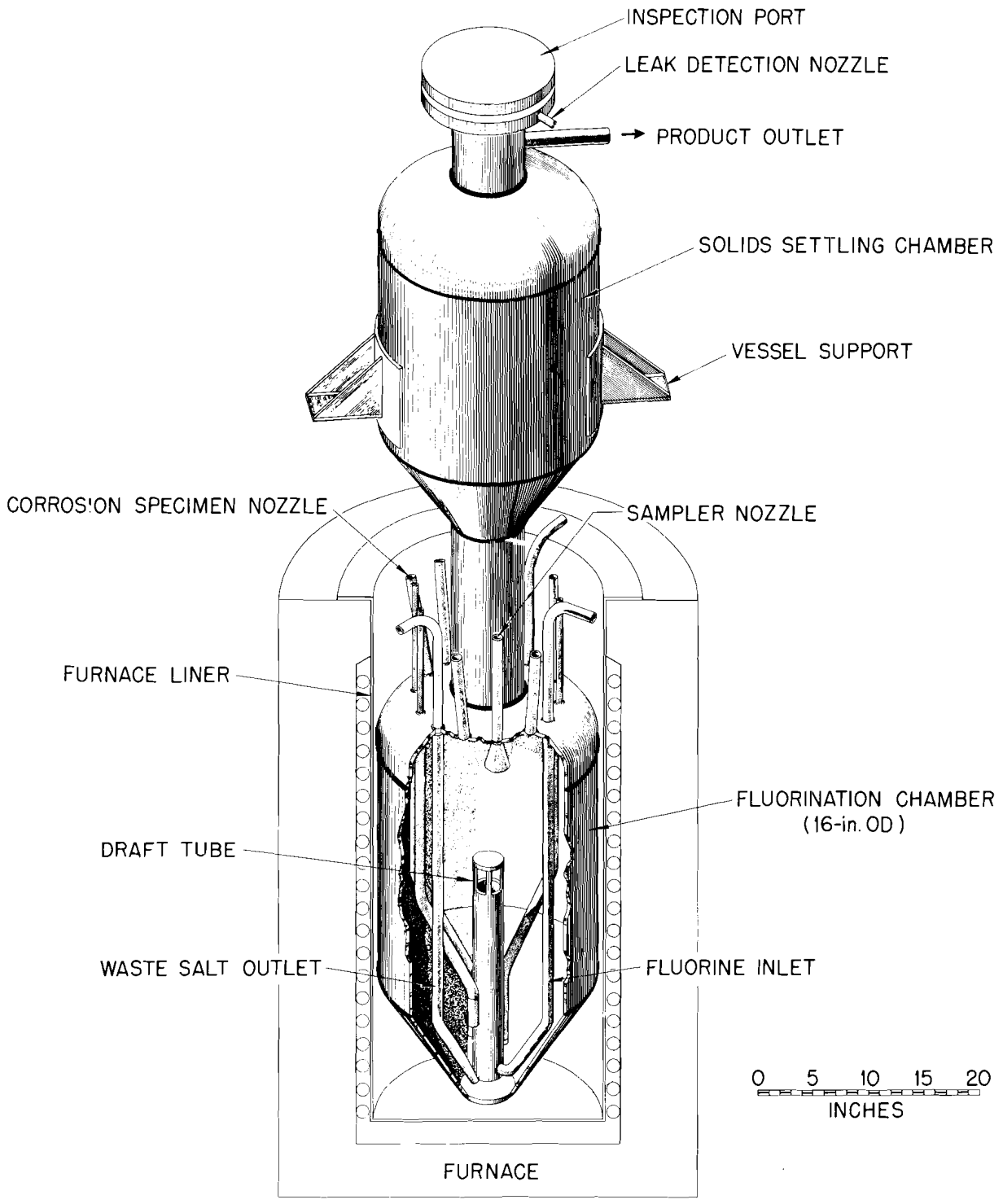

FIG. 11 FLUORINATOR

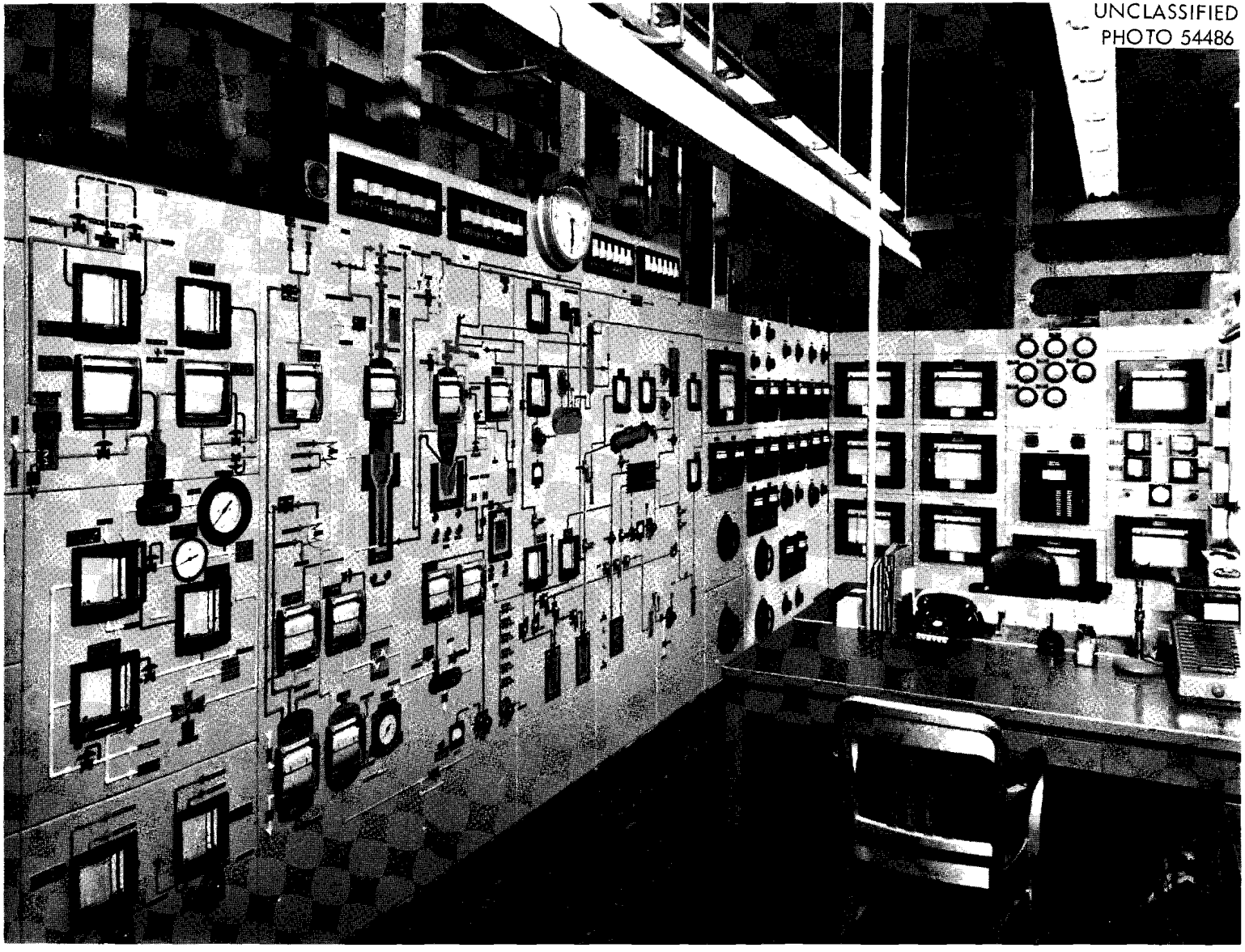

FIG. 12 VPP PANEL BOARD

flow rate of 150 g min, (c) the use of a movable-bed absorber (the fixed-bed absorbers will be available for emergency use), and (d) the use of a small product receiver to recover for sampling the UF_6 from each individual run followed by transfer of product from several runs to a larger shipping cylinder.

The first development runs were a series of seven runs (T-1 to T-7) with Zircaloy-2 simulated fuel elements, containing no uranium, weighing ~ 30 kg each. The purpose of this series was to study the HF dissolution, or head-end, phase of the plant. Studies included evaluation of the dissolution rate of Zircaloy in 37.5-37.5-25.0 mole % $NaF-LiF-ZrF_4$ salt at 650 to 500°C and the efficiency of HF utilization under various conditions. The dissolution rates, dissolution times, and average HF utilizations are reported (Table 1) based on 90% completion of the dissolution to eliminate the ambiguity often associated with evaluating the end of the dissolution.

The maximum temperatures were the initial dissolution temperatures. As the dissolution proceeded and the salt melting point decreased due to increased ZrF_4 concentration, the dissolver operating temperature was lowered to within 50°C of the salt freezing point. In some cases, the final ZrF_4 concentration was high enough (that is, above 45 mole%) that the temperature had to be increased above the minimum in the final stages. The twofold increase in dissolution rate in run T-7 is due to the fact that this was a two-element dissolution, while all preceding runs were single-element dissolutions.

Comparable data were obtained (Table 1) for dissolution of nonirradiated Zr-U alloy elements (runs TU-1 to TU-7). The first four of these runs were two-element and the other three single element. Although there was little difference in the fuel element length or surface area, some elements were about twice as heavy as others. In general, runs were performed with 40-50 kg of Zr-U alloy containing 500-600 g of uranium. Operating conditions were then selected after the runs on dummy fuel, viz. dissolution temperature range of 650-500°C and an HF flow rate of 150 g/min. The lower flow rate in run TU-6 was caused by operating difficulties.

The TU runs were complete flowsheet demonstration runs. In addition to providing additional data on fuel element dissolutions, these runs were also designed to evaluate the fluorination step (Table 2) and the absorption-desorption cycle since both operations are performed in new vessel geometries. In some runs (TU-4 through 7) two flow rates were used because of indications that fluorine utilization is better at low flow rates but that a high flow rate is necessary for a low final uranium concentration without prolonged

Table 1. SUMMARY OF VOLATILITY PILOT PLANT DISSOLUTION STUDIES

Run No.	Temp, °C Max	Temp, °C Min	Dissolution Rate*	Dissolution Time, hr**	HF Utilization g/min	HF Utilization avg %**
T-1	560	520	0.84	32.1	104	13.5
T-2	530	525	0.69	34.6	40	28.9
T-3	625	550	1.46	20.2	90	27.0
T-4	630	495	1.45	18.5	90	26.9
T-5	625	530	1.21	22.5	90	22.4
T-6	650	500	1.20	22.0	150	13.4
T-7	655	523	2.77	19.0	135	34.4
TU-1	670	490	2.46	18.2	92	44.5
TU-2	650	500	2.82	15.5	125	37.3
TU-3	655	594	3.22	12.3	150	35.8
TU-4	650	555	2.70	8.5	146	33.8
TU-5	650	500	2.50	15.7	150	24.5
TU-6	650	500	1.89	18.8	121	22.8
TU-7	650	500	3.68	10.8	150	35.7

* Average kg/hr to 90% completion.
** Based on 90% completion.

fluorination. Normally, fluorination is continued until the final uranium concentration in the salt is < 10 ppm, resulting in a total uranium loss to the waste salt of < 2 g.

Table 2. SUMMARY OF VOLATILITY PILOT PLANT FLUORINATION STUDIES
Fluorination temperature: 500±10°C

Run No.	U Conc., ppm salt* In	U Conc., ppm salt* End	F_2 Flow Rate SLM	F_2 Flow Time, min Used	F_2 Flow Time, min To give 10 ppm in salt	Loss, Wt %
TU-1	2830	1.2	12	150	77	0.07
TU-2	2040	3.8	6	150	55	0.28
TU-3	3003	9.1	9	105	75	0.31
TU-4	5118	5.6	4	75	97	0.16
			12	60		
TU-5	2205	1.0	4	60	85	0.05
			16	30		
TU-6	2667	0.7	6	60	80	0.04
			16	25		
TU-7	2201	4.2	6	60	95	0.06
			16	40		

* 27.5 mole % NaF, 27.5% LiF, and 45% ZrF_4

The next column in Table 2 is the total fluorine time (in minutes) required to achieve a U concentration of 10 ppm in the salt. These times were obtained by interpolation of analyses made at different time during fluorination. The losses shown in the last column represent a range of 0.18 to 1.9 grams uranium and consist of losses to the waste salt (based on final U concentration after fluorination) and to the caustic scrubber system.

Table 3 lists the chemical contaminants in the product from each small product cylinder prior to thermal transfer of the UF_6 to the standard shipping cylinder. The high sodium contamination in the earlier runs is probably present as NaF. Run TU-1 was the only run in which the fixed-bed absorbers were used. It appears likely that NaF fines were entrained in the gas stream in this run and that two more runs were needed to remove them from the system. No explanation has been proposed for the erratic behavior of copper and molybdenum.

Table 3. VOLATILITY PILOT PLANT PRODUCT IMPURITIES (ppm of UF_6)

Run No.	Cr	Cu	Fe	Li	Mo	Na	Ni	Sn	Zr	Total
TU-1	< 1	10	2	< 2	100	1300	3	2	< 1	< 1421
TU-2	< 1	17	< 1	< 2	69	600	< 1	1	< 1	< 693
TU-3	< 1	74	5	< 2	17	600	24	4	< 1	< 728
TU-4	1	210	6	< 1	21	< 10	4	4	< 1	< 253
TU-5	< 1	4	< 1	< 1	61	< 10	4	< 1	< 1	< 84
TU-6,7	< 1	8	2	< 1	220	< 10	6	2	< 1	< 251

Table 4 summarizes the Volatility Pilot Plant uranium inventory to date. The 261-g system residue is a "by difference" forced balance. System holdup can be determined only after a water wash of the system, which will be scheduled in the future. The only previous water wash of equipment after processing of UF_6 yielded 320 g of U, and the 261-g system residue is probably reasonable.[3]

Table 4. VOLATILITY PILOT PLANT URANIUM INVENTORY
(Runs TU-1 to TU-7)

	Uranium, g	
Fuel dissolved		3579
Uranium measured		
UF_6 product shipped	2849	
Trapped on NaF	337	
Samples for analyses	65	
Measured losses	5	
Product cylinder heels	62	
Total U measured out		3318
Difference (system residual)		261

FUTURE PROCESSING

The pilot plant is currently being modified to meet containment requirements. The chief building modifications will permit the required air flow and pressure controls and installation of a KOH scrubbing system for all off-gas, including cell off-gas. After containment work is completed and the new off-gas solids removal system installed, additional cold runs are scheduled to evaluate these improvements. Operations will then be started with highly irradiated long-decayed fuel. Eventually short-decayed fuel will be processed. In addition, flowsheets for processing other fuel materials such as stainless steels and oxides are being developed for future pilot plant programs.

REFERENCES

(1) Cathers, G. I., Nuclear Science & Engineering, 2, 768-77 (1957).

(2) Cathers, G. I., Jolley, R. L., Moncrief, E. C., Proceedings American Nuclear Society, Annual Meeting, Chicago, Illinois, June 1960.

(3) Carr, W. H., Chemical Engineering Progress Symposium Series, Nuclear Eng. -Part VIII, 56, 57-61 (1960).

(4) Milford, R. P., et al., Industrial and Engineering Chemistry, 53, 357-362, (May 1961).

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