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ORNL-3623
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CORROSION OF THE VOLATILITY PILOT PLANT INOR-8 HYDROFLUORINATOR AND NICKEL 201 FLUORINATOR DURING FORTY FUEL-PROCESSING RUNS WITH ZIRCONIUM-URANIUM ALLOY

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OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price $3.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Department of Commerce, Springfield, Virginia

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ORNL-3623

Contract No. W-7405-eng-26

Chemical Technology Division

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MARCH 1965

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CONTENTS

Page

Abstract 1

Introduction 2

Hydrofluorinator Corrosion 4

Description of Hydrofluorinator 4

Operating Environment 6

Typical Operating Conditions 6

History of Hydrofluorinator 10

Hydrofluorinator Corrosion Measurements and Results 11

Wall-Thickness Measurements 11

Air Oxidation of INOR-8 20

Corrosion of INOR-8 by Aqueous Cleaning Solutions 20

Surface Attack on the Hydrofluorinator Walls 21

Examination of the Lower 17 inches of the Hydrofluorinator 23

Corrosion of Molten Salt and HF Lines 28

Corrosion Measurements by Chemical Analyses 33

Fluorinator Corrosion 33

Description of Fluorinator 33

Operating Environment of Fluorinator 36

Typical Operating Conditions 37

Operating History of Fluorinator 41

Fluorinator Corrosion Measurements and Results 43

Bulk-Metal Losses 43

Fluorinator Pitting 47

Intergranular Corrosion 49

Page

Fluorinator Corrosion by Aqueous Cleaning Solutions..... 49

Air Oxidation of Nickel 201..... 57

Corrosion of Other Metals in the Fluorinator Environment..... 58

Discussion and Conclusions..... 60

Acknowledgement..... 63

Appendix..... 64

References..... 71

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ABSTRACT

Corrosion of the Volatility Pilot Plant process vessels was periodically determined during 40 processing runs in which uranium was recovered from both irradiated and nonirradiated zirconium and Zircaloy-2-clad fuel elements. The primary reaction vessels were the hydrofluorinator, constructed of INOR-8, which was exposed to gaseous hydrogen fluoride and an $NaF-LiF-ZrF_4$ molten salt mixture at 500 to 650°C, and the fluorinator, constructed of Nickel 201 (low-carbon nickel), which was exposed to fluorine and molten salt at about 500°C.

Both the hydrofluorinator and the fluorinator were designed with substantial corrosion allowances. Based on the corrosion allowance remaining and maximum bulk-metal loss rates, the vessels should be suitable for at least 28 additional runs and possibly considerably more. So far, 40 runs have been made.

Wall-thickness measurements were made primarily by ultrasonic measuring devices. Direct measurements were made by Vidigage, and remote measurements were made in the hydrofluorinator by a pulse-echo technique originally developed for use in the Homogeneous Reactor Test. Pitting, cracking and intergranular corrosion were studied visually with telescopes and mirrors, by radiography, by wax impressions, and by removal and examination of specimens. Hydrofluorinator corrosion rates were also determined from analyses of corrosion products in the salt. Corrosion data for Nickel 201 and other metal that had potential as fluorinator construction material were obtained from corrosion rods inserted in the fluorinator.

Corrosion in the INOR-8 hydrofluorinator occurred primarily by bulk-metal loss. Cracking occurred in the lower 17 in. of the vessel, making it necessary to replace this section after 29 runs; but this cracking is believed to have been due to weld stresses on a substandard piece of INOR-8. The maximum corrosion rate of 0.14 mil/hr of HF exposure (38 mils/month of molten salt) occurred in the replacement bottom. The maximum rate for the remainder of the vessel after 40 runs was 0.028 mil/hr of HF (8.1 mils/month of molten salt or about 0.7 mil per run). A few pits estimated to be not more than 20 mils deep or 20 mils in diameter, and several small fissures estimated to be not more than 10 mils wide, were seen in the lower section of the

hydrofluorinator after 40 runs, but no extensive corrosion was observed.

The Nickel 201 fluorinator had significant bulk-metal losses and intergranular corrosion. The weld filler metal 61 used for construction of the fluorinator was selectively attacked by aqueous solutions used to decontaminate the system. The maximum Nickel 201 bulk-metal loss of 0.9 mil/hr of F_2 exposure occurred in the lower vapor region after 14 runs. Two specimens cut from the lower fluorinator wall after 29 runs had a total corrosion rate (including intergranular corrosion on the inside and outside surfaces) of 0.28 to 0.56 mil/hr of exposure to F_2. Pits up to 10 mils deep were measured in the vapor section after 14 runs.

INTRODUCTION

The Fluoride Volatility Pilot Plant at Oak Ridge National Laboratory was used to demonstrate a nonaqueous process for recovering enriched uranium from spent fuel elements. From September 1960 through November 1963, forty runs were made with both irradiated and nonirradiated zirconium and Zircaloy-2-clad fuel. The process used gaseous hydrogen fluoride to dissolve the fuel element in an $NaF-LiF-ZrF_4$ molten salt mixture in the 500 to 650°C temperature range. This was done in the hydrofluorinator vessel which was constructed of INOR-8.[a] After the fuel element was dissolved, the molten salt was transferred to the fluorinator, where it was sparged with elemental fluorine to volatilize uranium from the salt as UF_6. The fluorinator was constructed of Nickel 201[b] and normally operated at 500°C. The hydrofluorinator and fluorinator were connected by INOR-8 pipe.

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[a]Nominal INOR-8 composition (wt %): 71% Ni, 16% Mo, 7% Cr, 5% Fe.

[b]Nickel 201 was formerly known as L (low carbon) nickel. Nominal composition (wt %): 99.5% Ni, 0.01% C, 0.2% Mn, 0.15% Fe, 0.005% S, 0.05% Si, 0.05% Cu.

The results of this study indicate that the equipment can tolerate 28 more runs, making a total of 68.

Because of the high corrosion potential of the system, corrosion rates of the hydrofluorinator, fluorinator, and associated lines were an important consideration in the successful operation of the process. Corrosion-rate measurements for the hydrofluorinator were made after 7, 14, 21, 29 and 40 runs. Measurements for the fluorinator were made after 14, 21, and 29 runs. Wall thicknesses were measured primarily by Vidigage[a] and by a pulse-echo method originally developed for use at the Homogeneous Reactor Test.[1] Pitting, cracking, and intergranular corrosion were studied by visual examination with a Questar telescope,[b] an Omniscope,[c] by wax impression, by radiography, and by specimen removal and examination. Chemical analyses of the salt from the first 14 runs were made to determine hydrofluorinator corrosion rates from corrosion products in the salt. Of particular interest was a study of the bottom 17 in. of the hydrofluorinator which was removed after 29 runs because a crack developed near thermocouple-weld beads. Also of interest were two 4-in.-diam sections trepanned from the lower part of the fluorinator after 29 runs. Aqueous solutions were used to clean and decontaminate the equipment before most corrosion measurements were made.

Corrosion results after 7, 14, and 21 runs have been reported previously.[2,3,4] The purpose of this report is to give corrosion results after 29 and 40 runs and to summarize corrosion results from the entire zirconium program.

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[a]Manufactured by Branson Instruments, Inc., Stamford, Conn.

[b]Manufactured by Questar, Inc., New Hope, Pa.

[c]Manufactured by Lerma Corp., Northampton, Mass.

HYDROFLUORINATOR CORROSION

Description of Hydrofluorinator

The hydrofluorinator was about 17-ft high and was constructed of rolled and welded INOR-8 plate (Fig. 1). The lower 9 ft, which held the fuel elements during dissolution, was 5-1/2 in. in outer diameter and was made from four 2-ft sections and one 1-ft section of rolled 1/4-in. plate welded together. Above this section was a 16-in.-high cone made from 1/2-in. plate. The salt interface was normally in the conical section. Above the cone was a 24-in.-OD vapor de-entrainment section made of 3/8-in. plate. The vessel was located in cell 1 of Building 3019 and had a 6-in.-diam pipe extending upward into the penthouse for fuel-element charging.

A distributor plate and 3/8-in. INOR-8 pipe were attached to the bottom of the hydrofluorinator for introducing HF into the vessel. A 1/2-in. INOR-8 pipe line was also attached to the bottom of the distributor plate for transferring molten salt to the fluorinator. A third 3/8-in. INOR-8 pipe entered the hydrofluorinator 27 in. above the cone and was used for charging feed salt.

The 5-1/2-in.-diam section, cone, and the lower 2 ft of the 24-in.-diam section of the hydrofluorinator were heated by a furnace that had six separately controlled heating zones. The top of the 24-in.-diam section was heated with tubular electric heaters held against the vessel with clips that were tack welded to the vessel. Temperature measurements were made with thermocouples located in a well inside the vessel and tack welded to the outside surface.

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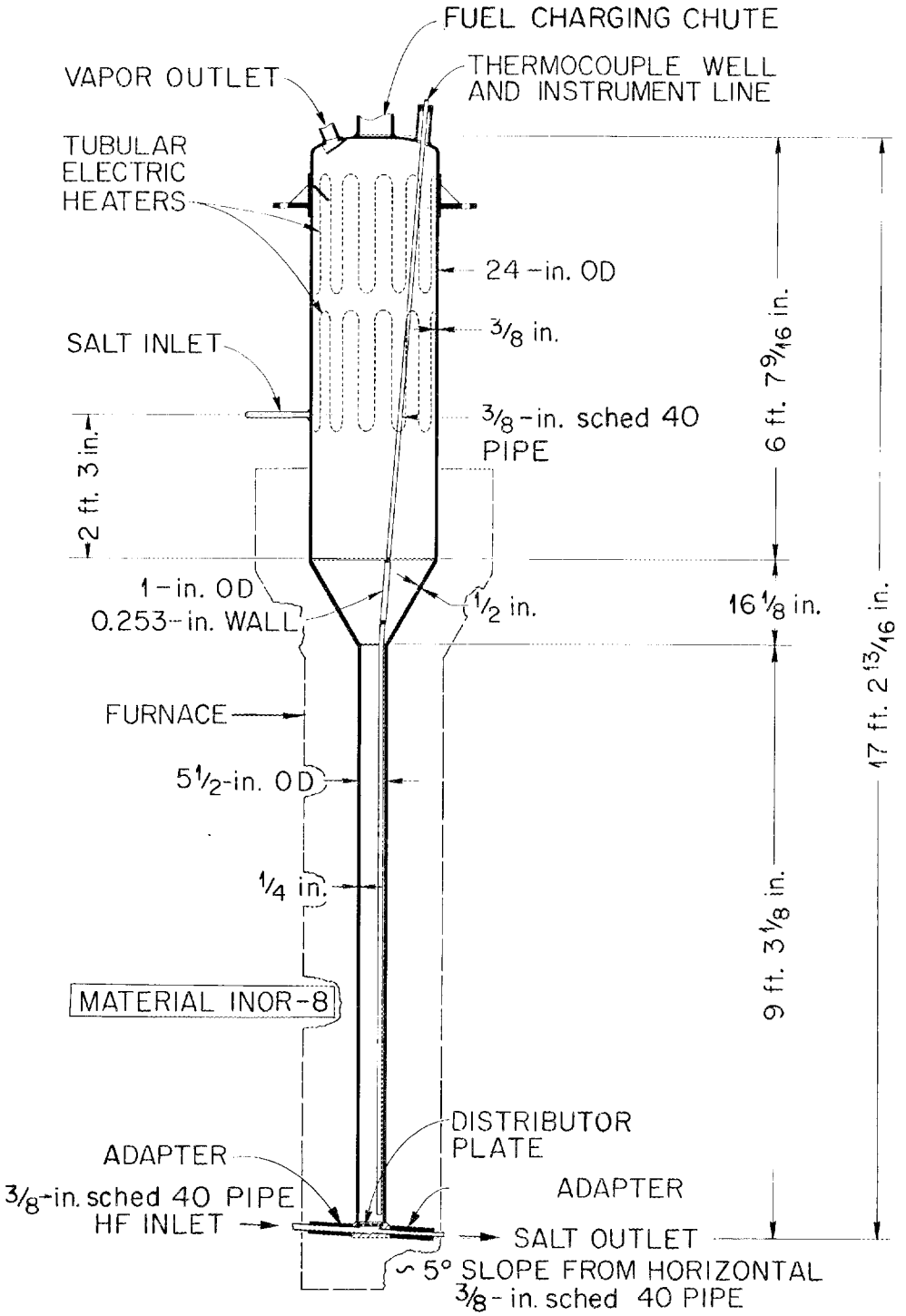

Fig. 1. Volatility Pilot Plant Hydrofluorinator.

The HF inlet line and the molten-salt transfer lines were heated by autoresistance heat generated by passing a low-voltage alternating current through the line.

Operating Environment

Four types of fuel elements were processed during the zirconium program, as follows: (1) dummy elements containing no uranium (designated as T-series runs), (2) nonirradiated elements containing about 1 wt % uranium (TU-series runs), (3) irradiated fuel cooled for about 6 years (R-series runs), and (4) irradiated fuel cooled from 6 to 13 months (R-series runs). In addition to fuel dissolution, the hydrofluorinator was subjected to molten-salt flushes and HF sparges for testing and cleaning the system (also designated as T-series runs). A summary of the run conditions for the zirconium program is given in Table 1.

Aqueous solutions were used for cleaning the system for inspection of the vessel walls and for reducing the radiation background. Ammonium oxalate solution (0.3 to 0.35 M) was used to remove the salt film, a solution of aluminum nitrate (0.01 to 0.24 M) and dilute nitric acid (0.01 to 0.8 M) were used for removing scale; sodium hydroxide-hydrogen peroxide-sodium tartrate solutions (5-1-1 and 5-2-2 wt %) were used for removing radioactive material such as ruthenium. Table 2 gives the decontamination conditions used during the zirconium program.

Typical Operating Conditions

The process was operated on a batch basis. Either one or two fuel elements were charged to the hydrofluorinator at room temperature. The vessel was then purged with helium and heated to about 650°C. The 24-in.-diam section was kept at 650°C for about 30 min to melt salt splash from

Table 1. Hydrofluorinator Run Conditions

Run Designation[a]	Salt Composition: NaF-LiF-ZrF_4 Mole % Initial	Salt Composition: NaF-LiF-ZrF_4 Mole % Final	Salt Composition: Uranium Content Wt %	Vessel Wall Temperature: Vapor Region Max	Vessel Wall Temperature: Vapor Region Min	Vessel Wall Temperature: Salt Region Max	Vessel Wall Temperature: Salt Region Min	Molten Salt Residence Time, hr	HF Flow[f] Rate g/min	HF Exposure Time, hr
Salt Transfer Studies	27-27-46	27-27-46	None	435	425	565	535	44.5	0	0
T-1[b]	43-22-35	31-17-52	None	410		560	520	87	104	38
T-2	38-30-32	30-27-43	None	380		530		95	40	41.5
T-3	39-39-22	31-26-43	None	575		625	550	57	90	25
T-4	38-37-25	30-27-43	None	590	500	630	495	51.5	90	22.5
T-5	38-37-25	30-27-43	None	570	460	625	530	62	90	27
T-6	38-37-25	31-30-39	None	550	390	650	500	59.5	118,150	26
T-7	37-37-26	27-27-46	None	590	440	655	525	53	135	23
					7 run Total			509.5		203
TU-1[c]	40-35-25	34-26-40	0.3	560	400	670	490	44	92	23
TU-2	37-38-25	30-27-43	0.2	620	450	650	500	35	125	24
TU-3	33-41-26	30-31-39	0.3	570	390	655	495	32.5	150	19.5
TU-4	42-34-24	37-29-34	0.5	575	440	650	555	36	146	11
TU-5	42-35-23	29-29-42	0.2	525	400	650	500	36	150	22
TU-6	38-37-25	34-28-38	0.3	525	385	650	500	35	121	19
TU-7	39-38-23	30-30-40	0.2	515	405	650	500	37	150	17
					14 run Total			765		338.5
T-8	28-30-42[d]	20-22-58	None	520	395	640	500	87	150	23.2
T-9	32-33-35	27-28-45	None	460	360	560	510	89	190	18.9
T-10	38-37-25	27-27-46	None	520	400	640	490	111	162	30.0
TU-8	35-41-24	28-32-40	0.2	525	400	652	495	49	150,110,40	18.0
TU-9	35-42-23	28-32-40	0.2	555	395	665	500	70	180,40	24.0
TU-10	36-40-24	29-31-40	0.2	520	395	650	495	129	150,40	22.8
TU-11	35-42-23	28-32-40	0.3	555	395	665	500	59	150,40	28.0
					21 run Total			1,359.0		503.4
TU-12	39-38-23	31-29-40	0.3	590	350	640	505	52	150,40	19.8
R-1	38-35-27	27-25-49	0.1	615	400	650	500	52	150,40	33.2
R-2	37-35-28	27-27-46	0.2	570	370	650	495	38	150,100,40	24.0
R-3	37-35-28	29-27-44	0.2	520	370	645	490	35	116,150,75,40	18.9
R-4	37-35-28	28-27-44	0.1	528	475	653	550	90	150,120,75,40	12.6
R-5	36-35-29	28-27-45	0.1	525	410	660	500	36	150,130,76,40	19.7
R-6	32-38-30	25-29-46	0.1	515	400	650	495	50	130,150,75,40	25.1
T-11	40-32-28	33-26-40	0.03	500	385	655	490	38	130,75,40	29.5
					29 run Total			1,750		686.2
TU-13	39-33-28	29-25-46	0.4	560	400	690	495	78.3	150,120,75,40	28.7
TU-14	39-32-29	30-24-46	0.2	636	385	660	500	62.8	150,120,100,40	28.5
TU-15	40-31-29	32-24-44	0.2	575	450	645	500	58.3	140,124,75,40	20.6
R-7	41-31-28	31-23-46	0.4	685	445	680	495	29.8	125,100,75,40	18.3
R-8	39-33-28	30-25-45	0.4	560	438	660	500	64.8	120,75,40	18.6
R-9	38-32-30	30-25-45	0.5	620	435	630	502	29.2	125,100,40	16.5
R-10	41-31-28	31-24-45	0.4	550	380	648	498	32.6	125,100,40	18.5
R-11	39-33-28	29-25-46	0.3	625	500	620	490	31.0	125,100,75,40	17.6
T-12	40-33-27	32-26-42	0.04	635	478	650	531	35.2	125,40	22.3
T-13	e		None	480		500		49.0	200	1.4
T-14	e		None	500		500		47.5	200	0.7
					40 run Total			2,268.5		877.9

[a] Runs are listed in chronological order.

[b] In the T-series simulated fuel elements of Zircaloy-2 were used.

[c] In the TU-series alloy fuels with Zircaloy-2 cladding was used.

[d] Abnormal final ZrF_4 content was due to an operational error.

[e] Salt was blended from 27.5-27.5-45 and 37.5-37.5-25 mole % NaF-LiF-ZrF_4 salts.

[f] HF flow rate was varied during dissolution to determine the effect of flow on dissolution rate. The 40 g/min rate was used for salt clean-up after dissolution was completed.

Table 2. Decontamination History of the Volatility Pilot Plant Hydrofluorinator

Cleaned After Run Number:	Cleaning Solution[a]	Time (hr)	Temperature (°C)
T-7 (7 runs)	0.35 M ammonium oxalate	41	95-100
	5 wt % HNO_3 - 5 wt % $Al(NO_3)_3$	10	95-100
TU-7 (14 runs)	0.35 M ammonium oxalate	4	60
	5 wt % HNO_3 (in lower 3 ft of vessel only)	3	25
	0.35 M ammonium oxalate	4	95-100
	5 wt % $Al(NO_3)_3$ adjusted to a pH of 3.5 with KOH	7	25
TU-11 (21 runs)	No cleaning was done		
T-11 (29 runs)	0.35 M ammonium oxalate (6 washes)	307 142	50-95 25
	0.03 M $Al(NO_3)_3$	70	50-95
	0.1 M $Al(NO_3)_3$	20 52	50-95 25
	0.1 M $Al(NO_3)_3$ - 0.01 M HNO_3 (2 washes)	93 11	50-95 25
	5,1,1 wt % NaOH, H_2O_2, sodium tartrate	10	25
	5,2,2 wt % NaOH, H_2O_2, sodium tartrate	20	25
T-14 (40 runs)	0.3 M ammonium oxalate (7 washes, circulated) (1 wash, static)	307 123 92.5	25-80 80-95 25
	Detergent solution[b] (2 washes)	3 18	25-80 80-95
	0.1 M $Al(NO_3)_3$ - pH 3.5	3.2 15.2	25-50 50
	5-1-1 wt % NaOH, H_2O_2, sodium tartrate	20	25

[a]Water rinses are not included in this table.

[b]Approximately 1.25 lb of dishwasher detergent in 350 gal of water.

the previous run. After the meltdown, heaters on this section were turned off. The feed-salt transfer line was heated to about 650°C, and 37.5-37.5-25 mole % NaF-LiF-ZrF_4[a] was charged to the hydrofluorinator, filling the 5-1/2-in. section and part of the conical section. After the salt transfer, only the cone, the 5-1/2-in.-diam section, and the HF line were heated. Anhydrous hydrogen fluoride vapor was introduced at the bottom of the hydrofluorinator at 40 to 190 g/min. Unreacted (excess) HF was recycled during the dissolution. In most runs, the remaining HF inventory was discarded after the run, and fresh material was charged for the next run. Commercial HF was charged to the system by distillation to reduce the sulfur content. Typical HF analyses are given in Table 1A in the Appendix. As the dissolution proceeded and the ZrF_4 content of the salt increased, there was a corresponding decrease in the melting point of the salt. The operating temperature of the hydrofluorinator was reduced to keep the temperature about 50°C above the melting point of the salt.[b] This was done to reduce corrosion. After dissolution was completed, the system was sparged with HF at 40 g/min for 2 hr to dissolve metallic impurities that might cause plugging of the molten-salt transfer lines. The molten salt was then sparged for an hour with N_2 to remove HF. A salt freeze valve in the transfer line between the hydrofluorinator and fluorinator was then melted, and the molten salt was transferred to the fluorinator, leaving only a small heel in the hydrofluorinator. The

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[a]The salt was previously purified to about 400 parts per million impurities at Y-12 plant. Private communication with F. A. Doss, June 3, 1964.

[b]The initial melting point of the salt was about 610°C, and the final was about 450.

hydrofluorinator furnace heat and the salt-transfer-line autoresistance heat were shut off, and a freeze valve was allowed to form in the transfer line. A summary of typical operating conditions of the hydrofluorinator is given in Table 3.

Table 3. Typical Hydrofluorinator Operating Conditions During Zirconium Processing

Hydrofluorinator Condition	Typical Time Required per Run (hr)
Heat up to 650°C, no salt or HF[a]	12
At 650°C without salt or HF	3
At 650°C with salt but no HF	4
At 650°C with salt, HF and Zr	3
Cooling from 650°C to 500°C with salt, HF, and Zr	14
At 500°C with salt, HF and Zr	4
At 500°C with salt and HF but no Zr	3
At 500°C with salt but no HF or Zr	6
Cooling from 500°C to 100°C without salt, HF, or Zr	20

[a]There was usually a small salt heel from the previous run.

History of Hydrofluorinator

The hydrofluorinator and associated lines were installed new at the start of the zirconium program. Inconel pipe (3/8 in., sched 40) was used originally for the HF and salt transfer lines. After TU-6 (13 runs), a crack, caused by salt expansion during heating, developed in a 12-in.-long INOR-8 adapter that connected the molten-salt transfer line to the hydrofluorinator at the bottom of the vessel. This adapter and the one for the HF inlet line were replaced with 3-in.-long adapters. After TU-7 (14 runs), the Inconel pipe on the HF line had corroded severely, and this line and the molten-salt transfer line were replaced with 3/8-in. sched-40 INOR-8 pipe. After run TU-8 (18 runs), piping was modified, and

the salt-transfer line between the hydrofluorinator and fluorinator was replaced with 1/2-in. sched-40 INOR-8 pipe (the larger pipe size was used because of its availability at that time). After TU-11 (21 runs), the thermocouple well and dip tube inside the hydrofluorinator, which originally extended to the bottom of the hydrofluorinator, were shortened so they extended only to the bottom of the conical section. This was done to more easily charge fuel elements into the lower section. After T-11 (29 runs), a crack was discovered between two thermocouple-weld beads about an inch above the bottom of the hydrofluorinator. The distributor plate and 14 in. of the 5-1/2-in.-OD section directly above were removed and replaced with a new distributor plate and a 14-in. section of 5-in. sched-40 INOR-8 pipe. About 4 ft of the HF line and molten-salt line were also replaced at this time. After TU-14, the feed-salt line was routed through a larger cell hole to allow more complete insulation of the line; this eliminated cold spots in the autoresistance-heated line.

Hydrofluorinator Corrosion Measurements and Results

Wall-Thickness Measurements

Hydrofluorinator wall-thickness measurements were made by a Vidigage in every instance except after 40 runs. The Vidigage is an ultrasonic measuring instrument having an accuracy of about ±1%. It measures the predominant wall thickness (not sparsely located pits) and was used to indicate the loss of bulk metal. This method required placing a probe against the surface to be measured and therefore was usable only when access was possible, such as during nonradioactive runs or after vessel decontamination.

After 7 runs, Vidigage measurements were made of the hydrofluorinator before and after it was cleaned with an aluminum nitrate-nitric acid

solution, which caused only negligible corrosion.[2] The vessel was cleaned prior to Vidigage readings taken after 7, 14, and 29 runs. However, no cleaning was done prior to the wall-thickness measurements made after 21 runs.

After 40 runs, the hydrofluorinator was only partially decontaminated, and wall-thickness measurements were made with the ultrasonic pulse-echo procedure originally developed for the Homogeneous Reactor Test.[1] With this method, a crystal transducer was placed inside the hydrofluorinator, which was filled with water to couple the transducer to the wall. The transducer emitted ultrasonic pulses that produced reverberation in the vessel wall at a point opposite the transducer. The time between pulses from these reverberations was measured by an electronic gating circuit and counter and was converted directly into wall thickness. This method also indicated predominant wall thickness. An estimate of the error of the pulse-echo system, based on time constants in the electronic circuitry, is ±3.3% for 1/4-in. material and ±2.5% for 1/2-in. material; however, the error could be as high as ±10%.[5] The variation of duplicate measurements taken in the 3/8-in. large-cylinder section of the hydrofluorinator is shown in Fig. 1A in the Appendix. These measurements have a maximum variation of 5 mils or 1.3% of the wall thickness.

The pulse-echo method was particularly suited to the hydrofluorinator since measurements could be made through the fuel-element-charging line from a low-radiation background area. The instrument could be adjusted to measure thickness of the vertical walls and the 60° conical section. Also, this method did not require insulation removal for access to the vessel, a necessity with Vidigage measurements.

In addition to wall-thickness measurements of the hydrofluorinator, data on metal losses were obtained by micrometer measurements of 3/8-in. sched-40 INOR-8 thermocouple and instrument lines removed from the hydrofluorinator after 21 runs.[4,6] These two lines extended the entire length of the vessel. The 1-in.-OD sections of the lines located in the conical section (see Fig. 1) were not measured since the original diameters were not accurately known. However, these sections showed no signs of abnormal corrosion.

In general, the hydrofluorinator was divided into four areas for corrosion study, as follows: (1) The upper cylinder (24-in. OD with a 3/8-in.-thick wall), which was exposed largely to vapor and salt splash and was operated at a generally lower temperature than the remainder of the vessel; (2) the conical section (1/2-in. wall), which was the normal interface area and was therefore exposed to both vapor and salt; (3) the upper 94 in. of the 5-1/2-in.-diam section (1/4-in. wall), which was normally filled with salt and which held the fuel elements during dissolution; and (4) the lower 14 in. of the 5-1/2-in.-OD section, which was replaced after 29 runs and which had shown somewhat higher corrosion rates than the remainder of the 5-1/2-in.-diam section.

Table 4 shows the maximum and average wall-thickness losses and corrosion rates based on HF exposure and molten-salt residence time for measurements made after different runs.[a] Note that in some runs measurements were made in only one quadrant and for only certain portions of the vessel due to inaccessibility of certain areas. The table shows only the

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[a]Corrosion rates based on molten salt exposure time include the periods during which HF was present in the system.

Table 4. Wall-Thickness Loses in the Hydrofluorinator During Zirconium Processing

	Number of Runs	HF Exposure (hr)	Molten Salt Exposure (hr)	Wall Thickness Loss[a] (mils) Max	Wall Thickness Loss[a] (mils) Avg	Corrosion Rate (mils/hr of HF exposure) Max	Corrosion Rate (mils/hr of HF exposure) Avg	Corrosion Rate (mils/month of molten salt exposure)[d] Max	Corrosion Rate (mils/month of molten salt exposure)[d] Avg
24-in.-diam Section									
24-in.-OD section	40	877.9	2,268.5	25	10.1	0.028	0.012	8.1	3.3
24-in.-OD section (lower 21 in. of the north wall only)	29	686.2	1,750	12	10.5	0.017	0.015	5.0	4.4
24-in.-OD section (lower 21 in. of the north wall only)	21	503.4	1,359	13	10.6	0.026	0.021	7.0	5.7
Instrument line from 24-in.-OD[b] section	21	503.4	1,359	7	3.2	0.014	0.006	3.8	1.7
Thermocouple well from 24-in.-OD[b] section	21	503.4	1,359	7	3.3	0.014	0.007	3.8	1.8
24-in.-diam section	14	338.5	765	18	6.0	0.053	0.018	17.2	5.7
24-in.-diam section (lower 21 in.)	7	203	509.5	11	9.3	0.054	0.046	15.8	13.3
Conical Section									
Conical section	40	877.9	2,268.5	25	15.3	0.028	0.017	8.1	4.9
Conical section (north wall only)	29	686.2	1,750	11	8.0	0.016	0.012	4.[illegible]	3.3
Conical section (north wall only)	21	503.4	1,359	16	12.4	0.032	0.025	8.6	6.7
Conical section	14	338.5	765	16	10	0.047	0.030	15.3	9.6
Conical section	7	203	509.5	10	4.2	0.049	0.021	14.3	6.0
Upper Part of 5-1/2-in.-diam Section									
Upper part of 5-1/2-in.-OD section	40	877.9	2,268.5	21	10.3	0.023	0.011	6.8	3.3
Upper part of 5-1/2-in.-OD section (north wall only)	29	686.2	1,750	16	9.8	0.022	0.014	6.7	4.1
Upper part of 5-1/2-in.-OD section (north wall only)	21	503.4	1,359	13	7.3	0.026	0.015	7.0	3.9
Instrument line from upper[b] 5-1/2-in.-OD section	21	503.4	1,359	12	7.0	0.024	0.014	6.5	3.8
Thermocouple well from[b] upper 5-1/2-in.-OD section	21	503.4	1,359	11	6.0	0.022	0.012	5.9	3.2
Entire 5-1/2-in.-OD section	14	338.5	765	12	4.0	0.035	0.012	11.5	3.8
Entire 5-1/2-in.-OD section	7	203	509.5	11	0.7	0.054	0.003	15.8	1.0
Bottom Part of 5-1/2-in.-diam Section									
Lower 14 in. of 5-1/2-in. OD section (replacement bottom)	11[c]	191.7	318.5	27	8.7	0.14	0.045	38.0	12.3
Distributor plate holes (original plate)	29	686.2	1,750	23 to 31	----	0.03 to 0.04	—	9.6 to 12.9	----
Lower 14 in. of 5-1/2-in.-OD section (where no outside attack was present)	29	686.2	1,750	18	—	0.026	—	7.5	----
Lower 14 in. of 5-1/2-in.-OD section (where outside attack was present)	29	686.2	1,750	69	—	0.10	—	28.8	----
5-1/2-in.-OD section (6 to 18 in. from bottom)	21	503.4	1,359	16	11.1	0.032	0.022	8.6	6.0
5-1/2-in.-OD section (bottom 6 in.)	21	503.4	1,359	18	12.8	0.036	0.025	9.7	6.9
Thermocouple well (bottom 6 in.)[b]	21	503.4	1,359	26	17.0	0.052	0.034	14.0	9.1
Instrument line (bottom 6 in.)[b]	21	503.4	1,359	50	22.0	0.10	0.044	26.9	11.8

[a]Measurements were made vertically at 3-in. intervals in the north, south, east and west quadrants unless specified otherwise.

[c]Based on an original diameter of 0.675 in.

[e]The replacement bottom was used for runs TU-13 through U-14.

[d]Corrosion based on molten salt exposure includes the periods during which HF was present.

gross loss and does not include other attack, such as pitting or cracking, which will be discussed later. Since there was from 10 to 20 mils of variation in wall thickness of the same nominal-size material used in the hydrofluorinator wall, thickness losses were determined by subtracting the final value from the initial thickness measured at approximately the same point. Figure 2 is a profile of the gross metal loss after 40 runs. A profile of the loss after 29 runs is given in Fig. 2A in the Appendix.

After 40 runs, the 24-in.-diam cylindrical and conical section had a maximum thickness loss (excluding pits or cracks) of 25 mils and an average attack of about half the maximum. The small cylindrical section, excluding the bottom 14 in., had a comparable loss, with a maximum of 21 mils and an average of 10.3. In this section, the maximum corrosion rate since the fourteenth run appears to have reached a rate of about 0.024 mil/hr, based on HF exposure, and 6.7 mils/month based on salt-residence time. Measurements made of the 3/8-in. instrument lines removed after 21 runs agree well with the above rate (excluding the bottom 6 in.). Corrosion rates measured at various times showed more variation in the cone and large cylinder than in the small cylinder, possibly because of the smaller number of readings taken in those areas. However, a maximum rate of about 0.028 mil/hr of HF exposure and 8.1 mils/month of salt-residence time appears fairly consistent with previous measurements in the cone and large cylinder since the fourteenth run. The maximum corrosion rates for the hydrofluorinator after 40 runs are given in Table 5.

Corrosion of the bottom 14 in. of the hydrofluorinator must be considered in two parts since the original bottom was replaced after 29 runs. Measurements taken of the lower 14 in. of the original bottom after 7 and

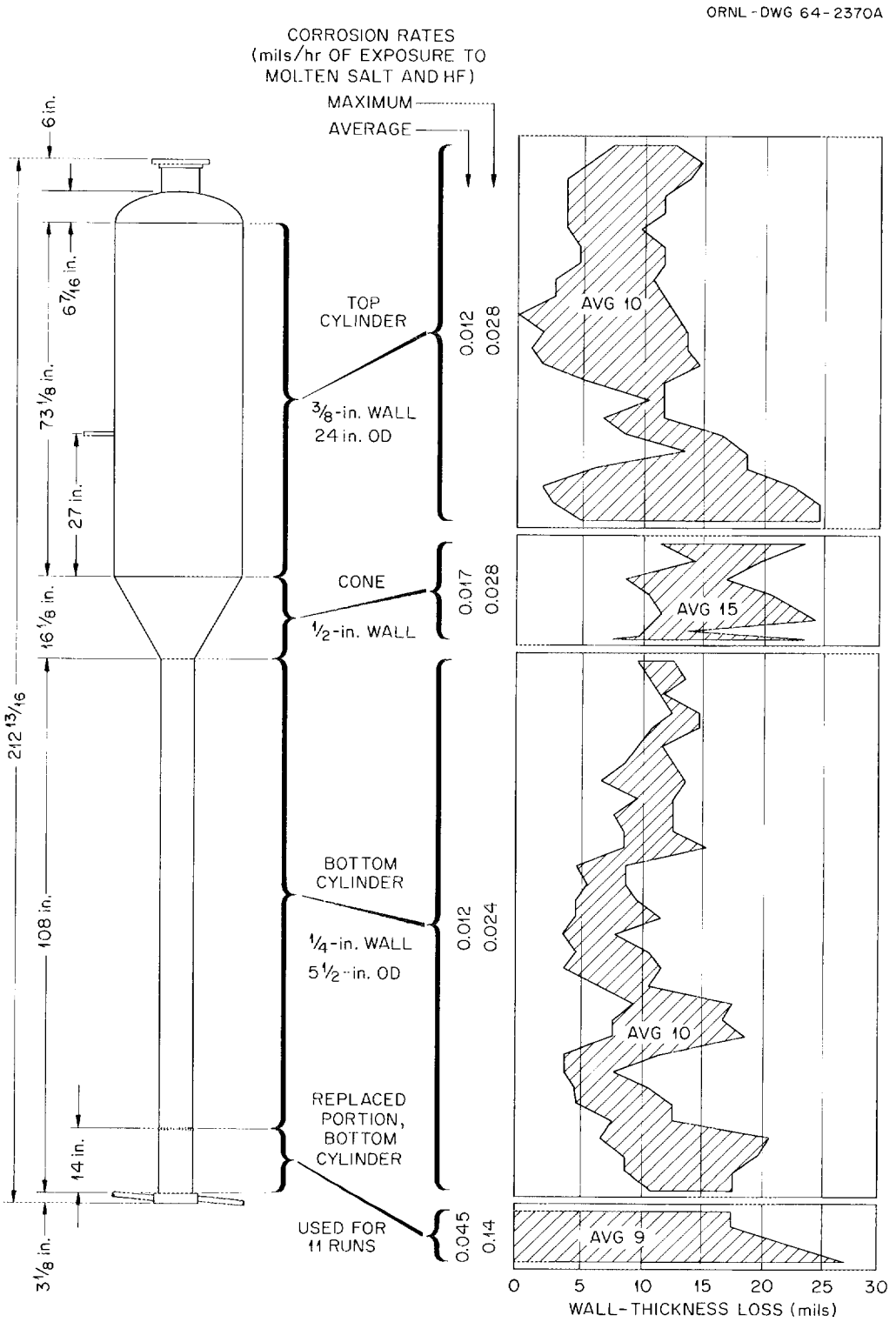

Fig. 2. Hydrofluorinator Wall-Thickness Loss During Forty Zirconium Processing Runs.

Table 5. Maximum Corrosion Rates in the Hydrofluorinator After 40 Runs

Location	Thickness Loss (mils)	Corrosion Rate (mils/hr of HF exposure)	Corrosion Rate (mils/month of molten-salt exposure)
24-in.-OD section	25	0.028	8.1
Conical section	25	0.028	8.1
5-1/2-in.-OD section (excluding bottom 14 in.)	21	0.023	6.8
Bottom 14 in. of 5-1/2-in.-OD section[a]	27	0.14	38.0

[a]Corrosion measurements are given for the replacement bottom, which was installed after TU-11 (used for 11 runs).

14 runs indicated corrosion rates comparable to those for the upper portion of the section. After 21 runs, the lower section showed a maximum attack of 18 mils (0.036 mil/hr of HF exposure), compared with a maximum of 13 mils (0.026 mil/hr of HF) for the upper portion. An instrument line removed at this time showed a maximum wall-thickness loss of 50 mils (0.10 mil/hr of HF) at a location about 1-1/2 in. above the distributor plate (Fig. 3). A thermocouple well removed at the same time showed a maximum loss of 26 mils (0.05 mil/hr of HF) at about the same location. This corrosion occurred in the vicinity of a clip that held the lines against the vessel wall. The higher corrosion rate at this location was apparently due to turbulence of the HF-salt mixture at that point since the upper section of the line showed only normal losses.

Vidigage measurements taken on the bottom 14 in. of the hydrofluorinator after 29 runs were complicated by corrosion of the outside surface, where salt had leaked through the cracked wall. Salt, in the presence of air, is more corrosive. In areas where no external attack occurred, the

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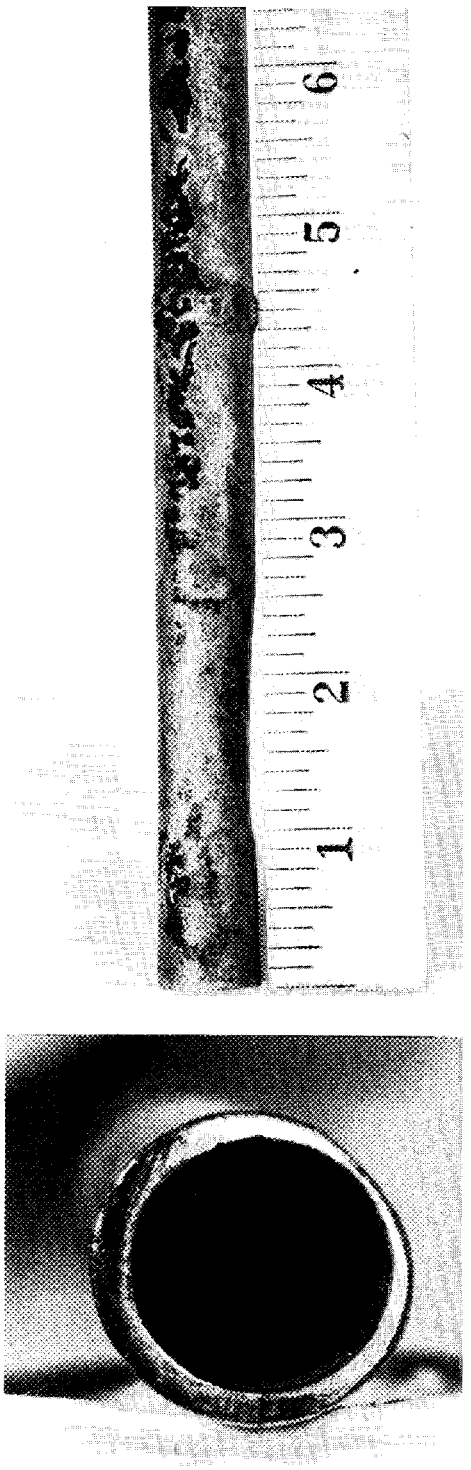


Fig. 3. Corrosion of an Instrument Line Removed From the Bottom of the Hydrofluorinator After Twenty-one Runs.

vessel showed only the normal corrosion rate, with a maximum loss of 18 mils (0.026 mil/hr of HF). However, where external attack occurred there was a maximum loss of 69 mils (0.10 mil/hr of HF).

The replacement bottom for the hydrofluorinator was made of 5-in. sched-40 INOR-8 pipe and was in use from run 30 through run 40. Wall-thickness losses in this area after 11 runs varied from negative values to a maximum loss of 27 mils (0.14 mil/hr of HF) and an average loss of 8.7 mils (0.045 mil/hr of HF). This was much higher than the rates for other parts of the hydrofluorinator during that period. However, there was a 28-mil variation in the thickness of the original wall of the replacement section, and, this, along with a possible instrument error of as much as ±10% (25 mils), could account for a large part of the unusually high rate in this section.

Since the maximum bulk metal loss for most of the hydrofluorinator was less than 28 mils, the possible instrument error and slight variations in the location of the points measured could result in an error that was a significant fraction of the total loss (although the precision of the measurements seemed good). However, these errors, based on the wall thickness remaining, are much smaller. Curves of the original wall thickness of the hydrofluorinator at 3-in. intervals vertically from top to bottom, starting at the top head weld are given for the north, south, east, and west quadrants in Figs. 3A through 6A (Appendix). The minimum wall thickness remaining (excluding pits, cracks, or intergranular corrosion) at the end of 40 runs in the large cylinder with its nominal 3/8-in. wall (excluding the top conical head, which was not measured) was 0.370 in. The conical section, with a nominal 1/2-in. wall, had a minimum thickness of 0.476-in. The upper small cylinder, with a nominal thickness of

1/4-in., had a minimum of 0.233 in. The lower 14 in. of the small cylinder, which had a nominal thickness of 0.272 in., had a minimum of 0.257. In all areas, the maximum losses (excluding pits or cracks) was less than 10% of the original wall thickness.

Air Oxidation of INOR-8

The rate of oxidation of INOR-8 in air is of interest since the exterior of the hydrofluorinator was exposed to air at high temperature (about 650°C) for long times. Studies were made at Battelle Memorial Institute (BMI) in which INOR-8 specimens were exposed to air at 700°C for 2000 hr.[7] A corrosion rate of 1.6 mils/month was obtained. There was a noticeable amount of flaking of the oxide scale. While the oxidation rate for the hydrofluorinator has not been measured separately (any metal losses would have been included in wall-thickness losses), there was no noticeable flaking of the exterior when the hydrofluorinator was examined after run T-11 (29 runs).

Corrosion of INOR-8 by Aqueous Cleaning Solutions

Three types of aqueous solutions were used in cleaning the hydrofluorinator system at various times during the zirconium program (Table 2). Ammonium oxalate solutions (0.3 to 0.35 M) were used for salt removal; nitric acid (0.01 to 0.8 M) aluminum nitrate (0.01 to 0.24 M) was used as a controlled corrodent for removing metallic scale; and 5-1-1 and 5-2-2 wt % sodium hydroxide-hydrogen peroxide-sodium tartrate solutions were used as complexing solutions to remove back-absorbed activity (mainly ^{106}Ru). Both Vidigage and laboratory studies were made to determine the amount of hydrofluorinator corrosion attributable to cleaning solutions.

Previous experience with ammonium oxalate solutions, such as those used in cleaning the hydrofluorinator, showed them to have a negligible

effect on INOR-8, and no further studies were done with ammonium oxalate solutions.[8] After run T-7, Vidigage wall-thickness measurements were made before and after the hydrofluorinator was cleaned for 10 hr with boiling 5 wt % HNO_3--5 wt % $Al(NO_3)_3$ solution. There was negligible wall-thickness change, within the accuracy of the instrument.[2]

Laboratory corrosion studies were conducted at BMI in which INOR-8 was exposed to alternating cycles of boiling 0.1 N $Al(NO_3)_3$--0.01 N HNO_3 and 5-2-2 wt % NaOH- H_2O_2-$NaC_2H_4O_6$ at room temperature, an exposure similar to that received by the hydrofluorinator.[9] Corrosion rates from 0.009 to 0.054 mil/month were measured for INOR-8 in the caustic-peroxide-tartrate solution. The aluminum nitrate-nitric acid mixture gave rates up to 11.5 mils/month during the first 3 hr of exposure, but the rate decreased to less than 3.1 mils/month after 19 hr, and to 1.5 mils/month after 84 hr. The cumulative corrosion rate for three aluminum nitrate-nitric acid cycles (120 hr) and two caustic-peroxide-tartrate cycles (40 hr) was less than 0.89 mil/month.

Based on the laboratory data, the wall-thickness loss from the hydrofluorinator due to the cleaning solutions used during the zirconium program was estimated to be less than 1 mil.

Surface Attack on the Hydrofluorinator Walls

Surface attack inside the hydrofluorinator, such as pitting and cracking, was observed by several methods during the zirconium program. At the end of TU-7 (14 runs), pit-depth measurements were made in the entire vessel by gamma radiography and in the 24-in.-diam section by replication with dental wax.[3,10] Gamma radiography with a ^{192}Ir source revealed only three areas of pitting. One was about 2-in. in diameter, located about 3 ft down from the top of the 24-in.-diam section. This

area had pits with a depth up to 7.5 mils. The other two areas that showed pitting attack were in the conical section about 6 in. below the top of the cone. These pits had a maximum depth of 10 mils.

Wax impressions capable of showing 0.1-mil irregularities were also made in the 24-in.-diam section after 14 runs. These impressions confirmed the presence of pits in this section. The maximum pit depth found was 8 mils. Many other pits were found, varying from 0.5 to 5.5 mils deep. Wax impressions were not made in the conical or 5-1/2-in.-diam sections. Both the wax replications and gamma radiographs showed the welds to be in good condition.

Metallography of the instrument line and thermocouple well, removed from the hydrofluorinator after 21 runs, revealed that the surface exposed in the vapor section was slightly roughened, with the grain boundary showing more attack than the grain.[6] The metal exposed to the interface region was very rough, while that exposed to salt was very smooth. Only one location, about 8 in. below the top of the hydrofluorinator, showed intergranular corrosion. The conclusion reached from the metallographic studies of these lines was that the INOR-8 lines were not selectively attacked by the hydrofluorinator environment. Additional information on hydrofluorinator surface attack was obtained from the metallurgical examination of the bottom section removed after 29 runs. This will be discussed in the following section.

Periodic observations of the inside of the hydrofluorinator were made with a Questar telescope (40 to 80 power) and an Omniscope (a low-magnification periscope) to look for areas of high corrosion. These observations were usually made after the system had been cleaned to remove the salt film. At the end of the 40-run zirconium program, the inside

surface of the 5-1/2-in.-diam section and the lower part of the cone section were inspected. This was done with a Questar telescope and mirrors. A few pits were seen in the 5-1/2-in.-diam section, such as the one shown in Fig. 4. The largest pit was estimated to be no more than 20 mils in diameter or 20 mils deep. Several small fissures were seen in the conical section, running upward from the lower weld. These fissures (Fig. 5) were estimated to be not more than 10 mils wide, and they did not appear to be very deep. Welds in the lower part of the hydrofluorinator appeared to be in good condition. No areas of extensive pitting or cracking were seen.

Examination of the Lower 17 inches of the Hydrofluorinator

After run T-11 (29 runs) the hydrofluorinator was decontaminated, and a visual inspection was made of the exterior. This examination revealed a salt leak in the 5-1/2-in.-OD section of the vessel just above the girth weld joining the distributor plate to the 5-1/2-in. section. The crack, shown in Fig. 6, occurred in the heat-affected area of two stainless-steel-sheathed thermocouple weld beads. The leakage was through two intersecting cracks. The horizontal crack was 1-1/8 in. long and was located between the thermocouple heads and the girth weld at the distributor plate. The vertical crack was 3/8 in. long and was between the two thermocouple heads. Both cracks were intergranular and appeared to have originated at the exterior. Only a small quantity of salt had leaked through the crack and covered about a 6-in.-diam circle on the exterior. The exterior of the hydrofluorinator and the thermocouples in the area of the leak were severely corroded, as is normal with metals in contact with molten fluorides in air. Since thermocouple failure occurred during run R-1, presumably the crack

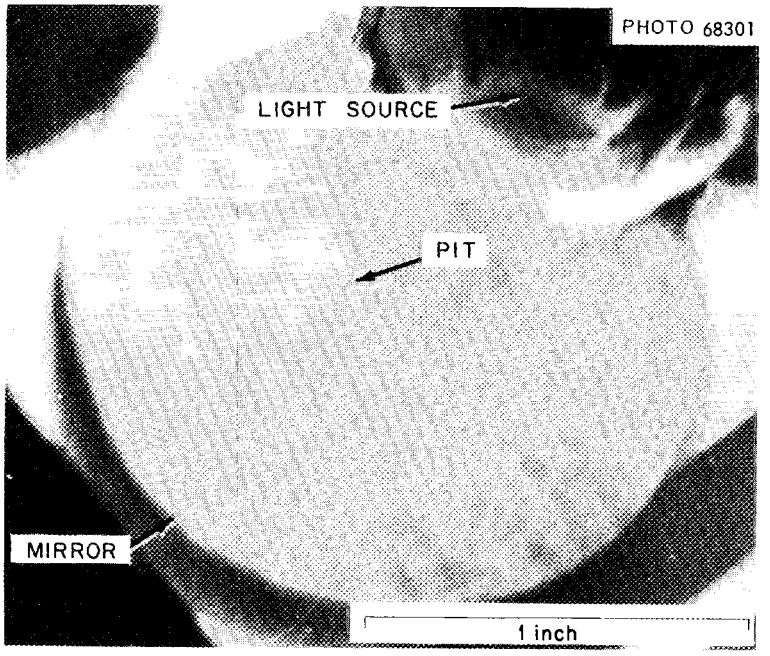


Fig. 4. A Pit Observed in 5-1/2-in.-OD Section of the Hydrofluorinator After Forty Runs.

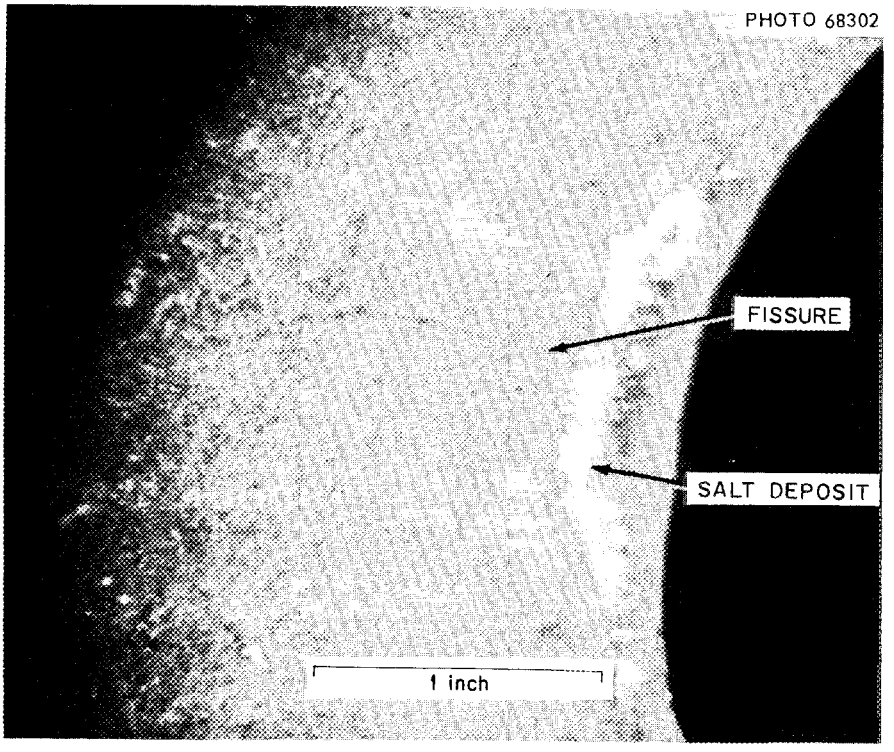
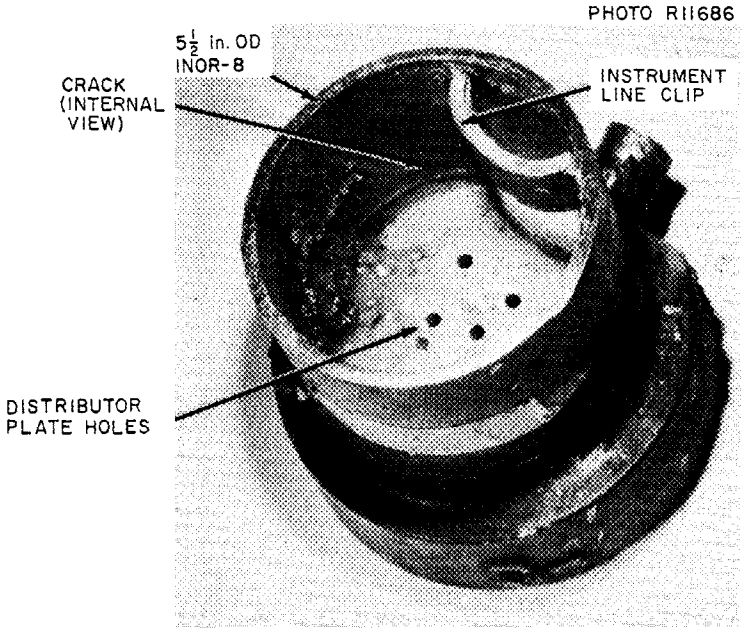


Fig. 5. Fissure in the Conical Section of the Hydrofluorinator After Forty Runs.



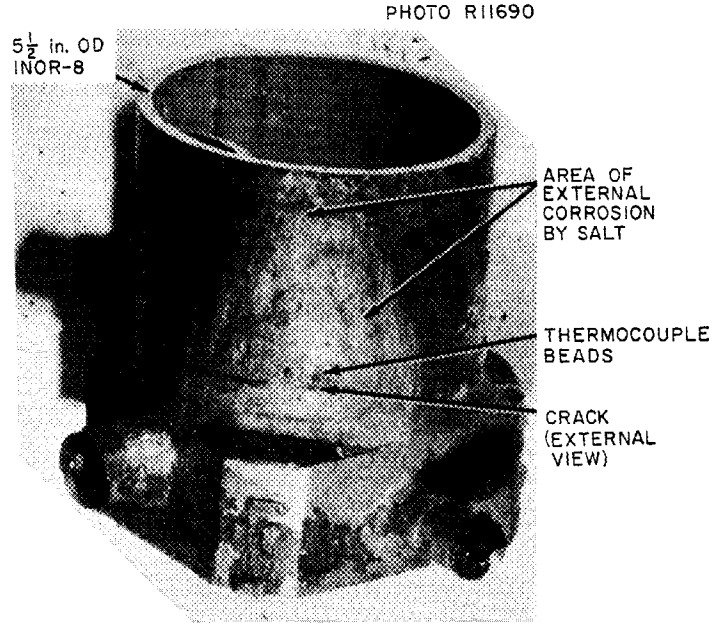


Fig. 6. Lower Section of Hydrofluorinator After Failure by Cracking (After Twenty-nine Runs).

also occurred then, and the salt sealed the crack sufficiently to permit continued operation.

The lower 17 in. of the hydrofluorinator was removed for metallurgical examination.[11] No gross bulging was found in the bottom section, and test specimens removed from this section showed no loss of tensile strength or brittleness of the INOR-8. However, chemical analyses indicated that it apparently was from an INOR-8 heat (SP-26) known to be susceptible to weld cracking.[12] Other intergranular cracks, up to 65 mils deep, were found on the exterior surface below the lower girth weld. Apparently the leak resulted from the effect of the thermocouple bead welds and the girth weld on substandard INOR-8, susceptible to weld cracking.

Many cracks between 10 and 40 mils deep were found on the inside surface of the vessel near the leak. These cracks, shown in Fig. 7, were classified into two groups. The first consisted of cracks perpendicular or adjacent to welds and were apparently associated with weld stresses. The second group contained horizontal cracks aligned in vertical rows throughout the lower 12 in. of the vessel. The horizontal cracks may have resulted from the rolling operation used in fabrication.

An important aspect of the internal cracking in the lower section of the hydrofluorinator was the possibility that cracking extended into the remaining 5-1/2-in.-diam section. Since the lower 9 ft of the hydrofluorinator was made from five separate cylinders welded together, it was possible that the part examined was not characteristic of the entire 5-1/2-in.-diam section. The portion of the vessel removed included one complete cylindrical section and about an inch of the second one. While a chemical analysis showed the two sections to have the same composition,

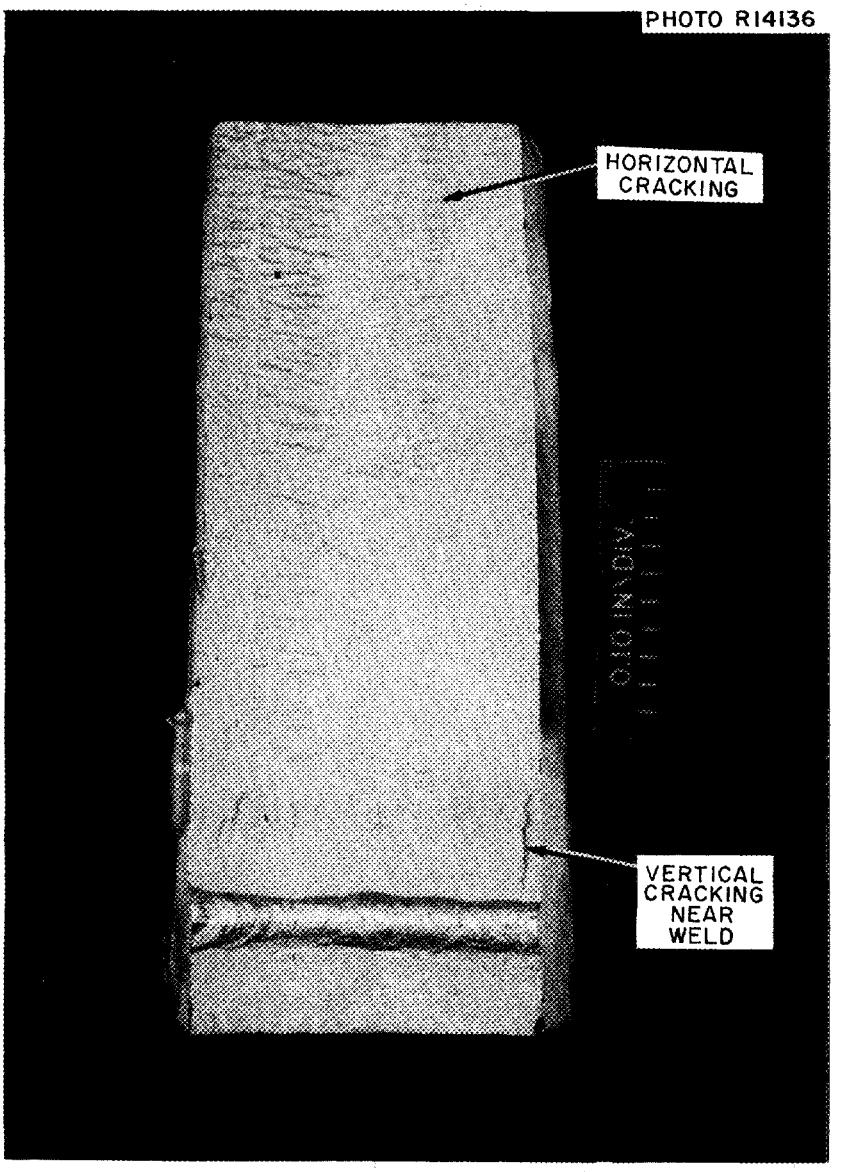


Fig. 7. INOR-8 Specimen Removed From the Bottom Section of the Hydrofluorinator After Twenty-nine Runs.

no cracking was seen in the upper section. Furthermore, visual examination of the remainder of the hydrofluorinator, using a Questar telescope, did not reveal extensive cracking such as was seen in the bottom section.

The distributor plate appeared to be in good condition, and no areas of extensive corrosion were seen by visual examination. All distributor-plate holes were open, and all holes except one were large enough to allow a 0.234-in. drill bit to enter, but none would pass a 0.25-in. bit. This indicates that the original 0.188-in.-diam hole had increased in diameter from 46 to 62 mils (a surface-thickness loss of 23 to 31 mils) during the 29 runs. This represents a corrosion rate of about 0.04 mil/hr of HF exposure, slightly higher than the general corrosion rate of the vessel.

Corrosion of Molten-Salt and HF lines

Generally, the molten-salt and HF piping in the system were exposed to less severe operating conditions than the hydrofluorinator. A possible exception was the HF inlet line, which was heated at all times that molten salt was in the hydrofluorinator. Molten salt as well as HF was present in the horizontal portion of the heated line near the hydrofluorinator. The salt-transfer line between the hydrofluorinator and fluorinator was normally near room temperature except when it was heated for making transfers. This was done once each run and required 2 to 4 hr to heat the line to about 550°C to make the transfer. After the transfer, a small quantity of salt was allowed to freeze in the line near the hydrofluorinator to form a seal (freeze valve).

The feed-salt transfer line, attached to the 24-in.-diam section of the hydrofluorinator, also remained unheated except during transfers. Feed-salt transfers were made once a run and required heating the line

for 2 to 4 hr at about 650°C. The line was purged with nitrogen the remainder of the time to keep out HF and radioactive material.

A rupture occurred after TU-6 (13 runs) in the 1-in.-OD adapter at the junction between the salt-transfer line and the bottom of the hydrofluorinator. This was the area where the freeze valve was formed. In addition to the rupture there were many other cracks on the outer surface (Fig. 8). Metallography revealed that the rupture and other cracks were intergranular and that they originated on the outside, indicating that they were caused by salt expansion.[13] Apparently this was a result of salt melting in the center of the freeze valve before the salt at each end became molten. The adapter was replaced temporarily until after TU-7, at which time 3-in.-long adapters were installed in both the salt transfer and HF inlet lines. The shorter adapter allowed more uniform heating, and no further difficulties were experienced. Portions of these 3-in.-long adapters were examined metallographically after they had been used for 15 runs (after T-11) and found in good condition.

Originally, all three autoresistance-heated lines that entered the hydrofluorinator were made of 3/8-in. sched-40 Inconel pipe. After TU-7 (14 runs) a leak developed in the HF line about 2 ft from the hydrofluorinator. Figure 9 shows a section of pipe in which the leak occurred. Metallography revealed that chromium and iron had been leached from the Inconel pipe in the vicinity of the leak. Leaching occurred all along the pipe but was less severe at greater distances from the hydrofluorinator.[13] Thinning of the pipe wall by corrosion apparently caused localized overheating (750°C maximum temperature) and even greater corrosion.

The 3/8-in. sched-40 Inconel pipe from the salt-transfer line between the hydrofluorinator and fluorinator showed much less corrosive attack

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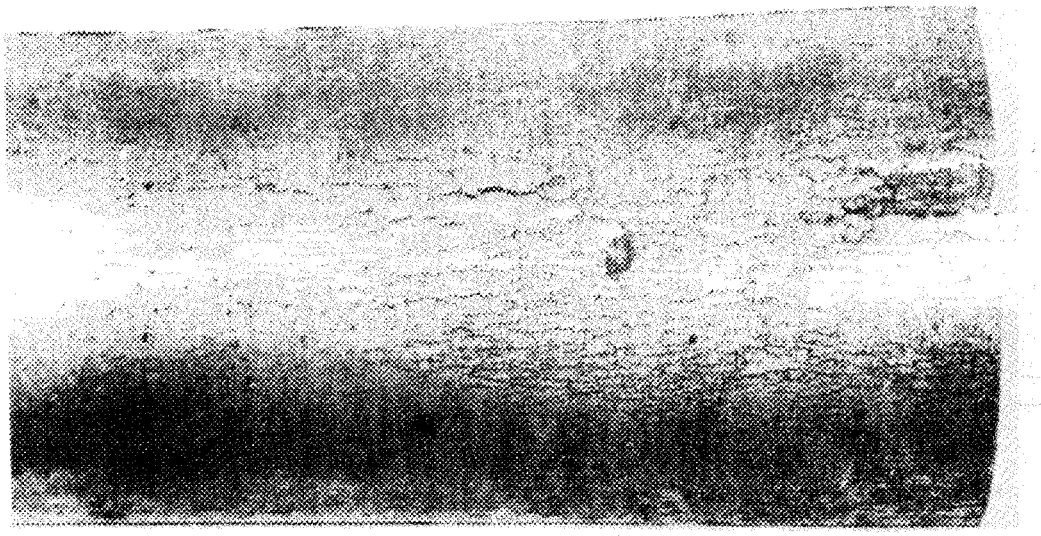

1/4 inch

Fig. 8. Cracking Due to Salt Expansion in an INOR-8 Adapter on the Hydrofluorinator HF Inlet Line.

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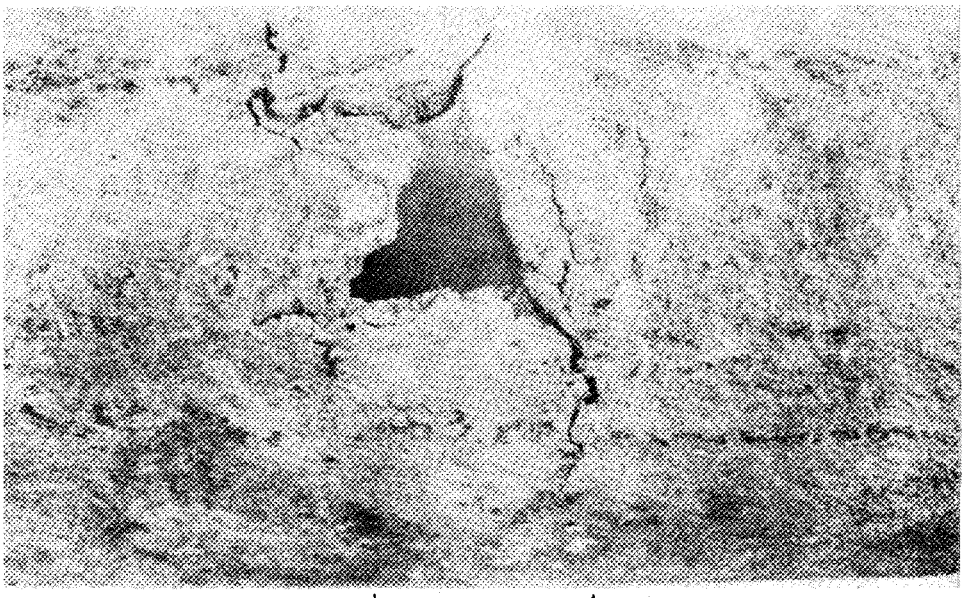
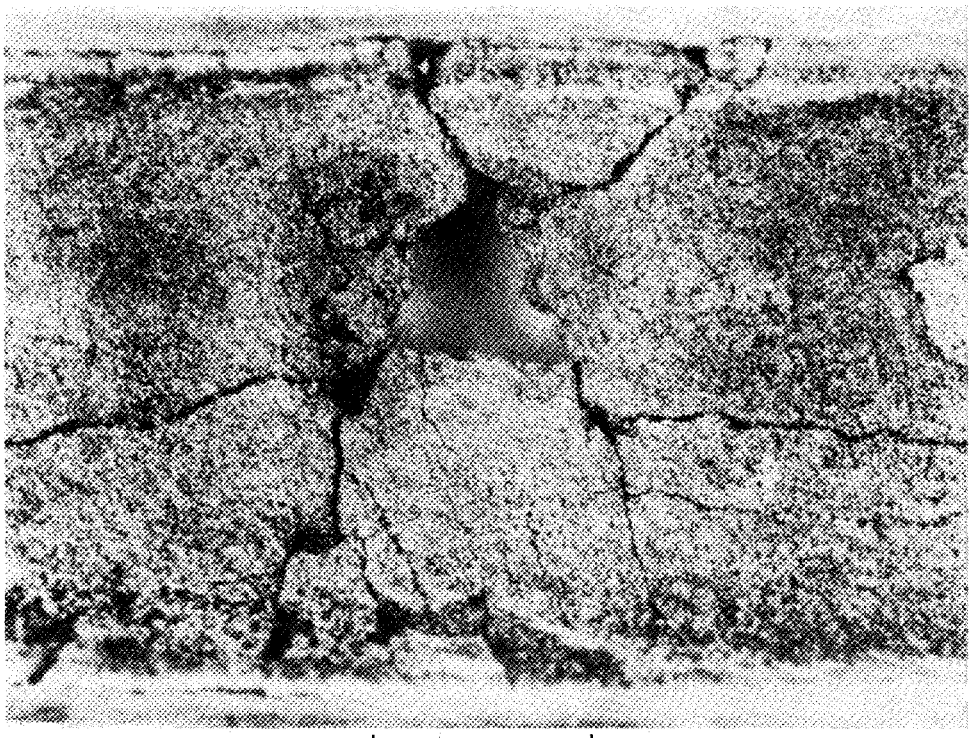


1/4 inch
Outside of pipe

BMI C-1498



1/4 inch
Inside of pipe

Fig. 9. Corrosion of Inconel Pipe in the Hydrofluorinator HF Inlet Line.

than the HF line; however, there was indication of metal loss, particularly in the areas closer to the vessels. The Inconel piping in the three auto-resistance-heated lines attached to the hydrofluorinator was replaced with INOR-8 pipe after TU-7 (14 runs).

After run T-11, corrosion measurements were made on both the 3/8-in. sched-40 INOR-8 HF inlet line and the 1/2-in. sched-40 INOR-8 salt-transfer line at the bottom of the hydrofluorinator. Sections approximately 4 ft long were removed from each line near the hydrofluorinator. Wall-thickness measurements were made by Vidigage, and a metallurgical examination was made by BMI.[14]

The inside surface of the HF line was roughened by corrosion products to a depth of about 3 mils, and there was a total wall-thickness loss of 6.4 mils (based on an original average wall thickness of 82.4 mils). Assuming that the line had received the same HF and molten salt exposure as the hydrofluorinator during the 15 runs in which it was used, the corrosion rate was 0.018 mil/hr of HF exposure and 6.5 mils/month of molten salt exposure. These rates are about the same as the average corrosion rates in the hydrofluorinator.

The section of the salt-transfer line removed after run T-11 showed no significant metallurgical change and little surface roughening.[14] Measurements of microsections indicated a 1- to 3-mil wall-thickness loss, while Vidigage measurements showed a 5- to 8-mil loss (based on an original wall thickness of 109 mils). This corrosion occurred during 11 runs or approximately 62 hr of molten salt exposure, while the line was heated for salt transfers.

Corrosion Measurements by Chemical Analyses

Metal loss from the hydrofluorinator wall during the first 14 runs was determined by analyzing the salt transferred to the fluorinator for the major constituents of INOR-8.[a] Material balances were made for nickel, iron, chromium, and molybdenum. Corrosion rates based on the total inside surface of the hydrofluorinator,[15-20] and HF exposure time are given in Table 6.

Corrosion rates based on nickel and molybdenum were lower than rates determined from Vidigage data. Nickel plated on the vessel walls and was removed only after acid washes. Significant amounts of molybdenum were seldom found in the process streams considered in the material balance.

Corrosion rate determinations based on chromium and iron were somewhat erratic from run to run. However, the average rate of 0.041 mil/hr of HF exposure, based on chromium, and 0.052 mil/hr HF exposure, based on iron, are in fair agreement with Vidigage rates taken after 14 runs (see Table 4).

FLUORINATOR CORROSION

Description of Fluorinator

The Volatility Pilot Plant fluorinator[b] was about 7 ft high and was made from 3/8-in.-thick Nickel 201 plate. Welds were made with filler metal 61[c]. The upper and lower sections of the vessel were 16 in. in outer diamter. They were joined by a 5-3/4-in.-OD center section, as shown in Fig. 10. Only the lower section contained salt. The center and

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[a]Nominal composition of INOR-8 (wt %) is: 71% Ni, 16% Mo, 7% Cr, 5% Fe.

[b]Also called the Mark III fluorinator.

[c]Nominal weld filler metal 61 composition (wt %): 93% Ni, 1.0% Fe, 0.25% Cu, 1.5% Al, 2.0 to 3.5% Ti, 0.15% C, 0.75% Si.

Table 6. Estimate of Hydrofluorinator Corrosion by Corrosion-Product Material Balance

Run No.	Corrosion Rate[a] in mils/hr of HF Exposure, Based on the INOR-8 Corrosion Products Below			
	Ni	Fe	Cr	Mo
T-1	0.003	0.013	b	c
T-2	b	0.007	< 0.012	c
T-3	< 0.001	0.073	0.036	c
T-4	0.009	0.044	0.031	c
T-5	< 0.004	0.033	0.026	c
T-6	0.004	0.031	b	< 0.004
T-7	0.013	0.091	0.030	0.013
Average		0.041	0.027	
TU-2	—	b	0.017	c
TU-3	0.003	0.051	0.097	0.0
TU-4	0.009	0.118	b	0.009
TU-5	0.004	0.045	0.041	0.002
TU-6	< 0.005	b	b	< 0.005
TU-7	0.006	0.083	0.077	0.024
Average		0.052	0.041	

[a]Corrosion rates are based on the entire inside surface area of the hydrofluorinator.

[b]Material balances were negative.

[c]Not determined.

ORNL-LR-DWG 39150 R3

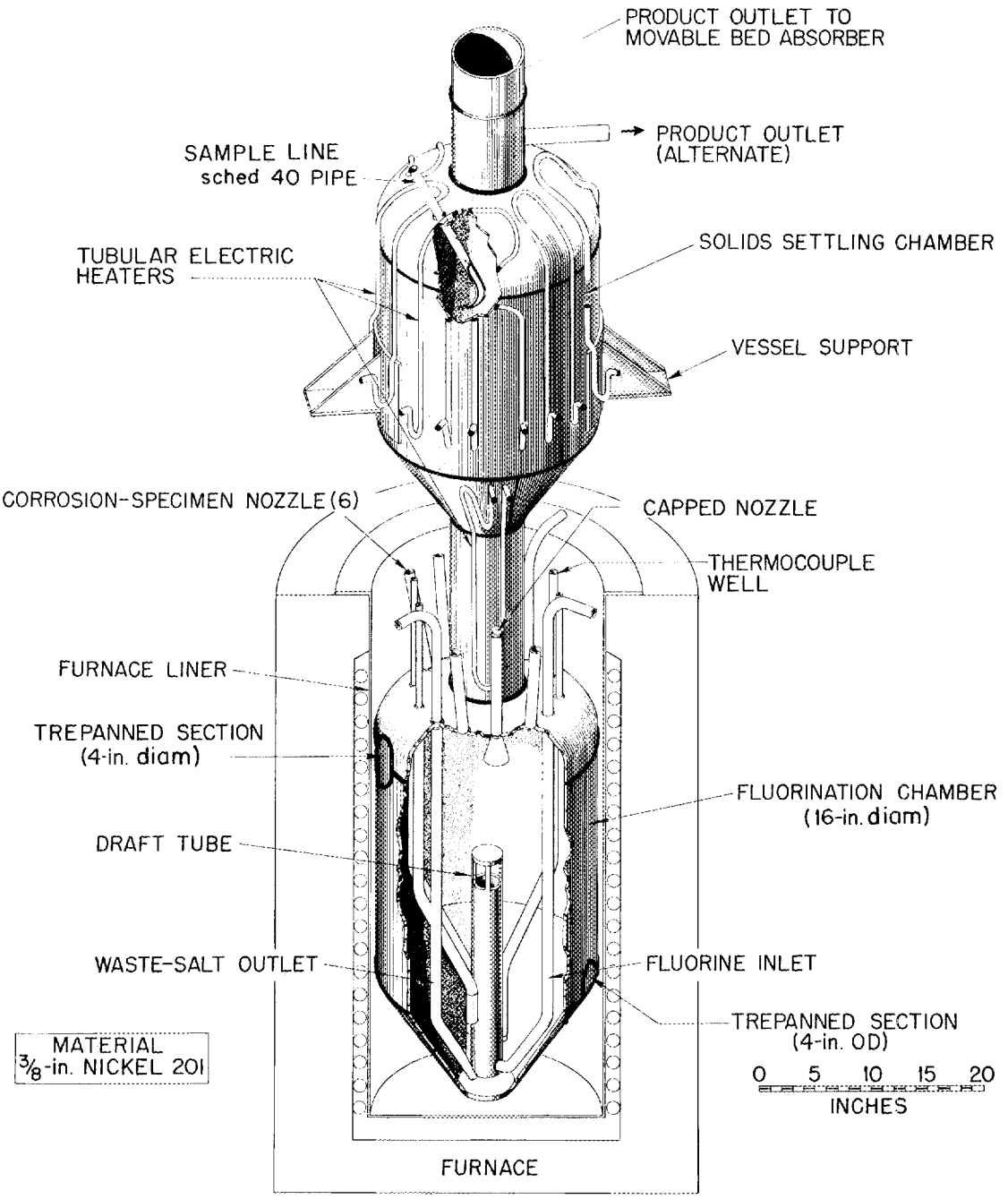

Fig. 10. Volatility Pilot Plant Fluorinator, Mark III.

upper sections were de-entrainment regions for removing solids from the gas stream that was discharged through the 5-in.-diam pipe at the top of the vessel. The center section formed a shelf above the lower section, through which piping and six 1/4-in.-diam corrosion rods entered the vessel.

The lower section contained a draft tube that provided intimate contact between salt and fluorine. Fluorine was introduced into the bottom of the draft tube through a 1/2-in. sched-80 nickel pipe. Waste salt was removed from the fluorinator through a second 1/2-in. sched-80 nickel pipe that extended to the bottom of the vessel. Salt samples were taken through a 1-in. sched-40 Inconel pipe that entered the vapor space in the upper section. An air-operated vibrator was attached to this line to aid in sampling. Uranium hexafluoride product from the fluorinator was collected in a movable-bed NaF absorber connected to the 5-in.-diam pipe at the top of the vessel.

The lower section of the fluorinator was heated by a single-zone furnace, which could be raised and lowered. The center and upper sections were heated separately by tubular electric heating elements attached by clips tack-welded to the vessel. These sections were covered with insulation. The temperature of the vessel was measured by thermocouples attached to the outer surface and by thermocouples inserted in a well in the lower section.

Operating Environment of the Fluorinator

The fluorinator was exposed to the following environments during the zirconium program: (1) salt transfers in which no uranium was present and no fluorine was used (T-series runs), (2) nonradioactive runs

in which uranium was fluorinated from the salt (TU-series runs), (3) radioactive runs with both 6-year- and 6- to 13-month-cooled elements (R-series runs), and (4) fluorine purges of the empty vessel for conditioning surfaces by forming a NiF_2 film that reduced the amount of conversion of UF_6 to UF_4 at the walls.

Aqueous solutions were occasionally used to clean the fluorinator for inspection or to reduce the radiation level. Here, ammonium oxalate solutions (0.3 to 0.35 M) were used to remove salt films from the interior surface. Metallic film was removed after T-11 (29 runs) with a 0.1 M aluminum nitrate--0.01 M nitric acid solution. However, the use of aluminum nitrate or nitric acid in the fluorinator was usually avoided due to the high corrosion rates on Nickel 201 and weld filler metal 61. Solutions of 5-1-1 and 5-2-2 wt % sodium hydroxide, hydrogen peroxide and sodium tartrate were used to remove activity from the fluorinator surface after runs T-11 (29 runs) and T-14 (40 runs).

The system was usually kept under a dry nitrogen atmosphere when not in use. After each cleaning or exposure to air, the vessel was fluorine-conditioned to reform the fluoride film on the inner surfaces. Conditioning was done by introducing a dilute mixture of fluorine in nitrogen and slowly increasing the fluorine concentration and temperature until normal operating conditions were reached. The operating conditions for the fluorinator during zirconium processing are given in Table 7, and the conditions for cleaning the vessel are given in Table 8.

Typical Operating Conditions

The fluorinator was operated on a batch basis. It was heated to operating temperature just prior to the salt transfer from the hydrofluorinator. The lower section was usually held at about 500°C, while

Table 7. Fluorinator Operating Conditions During Zirconium Processing

Run[a] Designation	Salt Composition NaF-LiF-ZrF_4 (mole %)	Salt Composition U (wt %)	Fluorination Temperature (°C) Salt	Fluorination Temperature (°C) Vapor	Molten Salt Residence Time (hr)	F_2 Rate (liters/min at 25°C and 1 atm)	Fluorine Exposure Time (hr)
F_2 conditioning	None		650-560	630-310	0	5 psig (static)	5.3
Salt-transfer studies	27-27-46	None	565-550	~375	49	0	None
T-1	31-17-52	None	555-540	175-150	38	0	None
T-2	30-27-43	None	570-545	180-150	78	0	None
T-3	31-26-43	None	550-525	170-160	94	0	None
T-4	30-27-43	None	515-485	340-325	15	0	None
T-5	30-27-43	None	580-550	375-360	27	0	None
T-6	31-30-39	None	575-560	480-375	15	0	None
T-7	27-27-46	None	605-580	360-340	18	0	None
F_2 sparge test	None		570-535	520-495	45	8	12.0
TU-1	34-26-40	0.3	505-500	360-350	52	12	2.5
TU-2	30-27-43	0.2	505-500	460-440	40	6	2.5
TU-3	30-31-39	0.3	510-500	330-320	38	9	1.75
TU-4	37-29-34	0.5	515-500	330-315	50	4,12	1.25,1.0
TU-5	29-29-42	0.2	510-500	360-325	36	4,16	1.0,0.5
TU-6	34-28-38	0.3	505-500	360-340	34	6,16	1.0,0.4
TU-7	30-30-40	0.2	510-500	360-340	65	6,16	1.0,0.7
Total					694		30.9
T-8	20-22-58	None	750[b]-525	590-340	141	0	None
T-9	27-28-45	None	715[c]-515	565-335	202	0	None
T-10	27-27-46	None	525-500	340-330	111	0	None
TU-8	28-32-40	0.2	500-495	360-330	54	6,16	1.7,0.3
TU-9	28-32-40	0.2	525-515	365-340	33	6	1.7
TU-10	29-31-40	0.2	505-500	360-340	60	6,18	1.7,0.4
TU-11	28-32-40	0.3	510-495	350-325	42	6,14	1.7,0.3
Total					1,337		38.7
TU-12	31-29-40	0.3	505-495	400-430	53	6,14	1.7,0.3
R-1	27-25-49	0.1	495-510	330-400	39	6,10,14	1.7,0.15,0.25
R-2	27-27-46	0.2	500	390-425	84	6,14	1.7,0.3
R-3	29-27-44	0.2	520	375-420	153	6,14	3.3,1.0
R-4	28-27-44	0.1	490	375-425	90	6,14	1.7,0.3
R-5	28-27-45	0.1	515	370-415	40	6,13.4	1.7,0.3
R-6	25-29-46	0.1	508-505	360-415	89	6,13	1.7,0.8
T-11	33-26-40	0.03	500-505	350-420	37	6,13	1.7,0.3
Total					1,922		57.6
TU-13	29-25-46	0.4	500-508	373-435	63.8	6,13	1.7,0.7
TU-14	30-24-46	0.2	500	340-378	52.8	6,13	1.7,0.3
TU-15	32-24-44	0.2	500	385-395	53.4	6,13	1.7,0.3
R-7	31-23-46	0.4	500	375-410	46.8	6,13	1.7,0.3
R-8	30-25-45	0.4	500[d]	360-450	71.0	6,13	1.8,0.6
R-9	30-25-45	0.5	500	345-375	45.1	6,13	1.7,0.3
R-10	31-24-45	0.4	500-505	340-385	81.5	6,13	1.7,0.3
R-11	29-25-46	0.3	500-507	330-375	52.6	6,13	1.5,0.3
T-12	32-26-42	0.04	498-510	375-510	64.4	6,13	1.7,0.6
T-13	e	None	500	325-500	24.8	0	None
T-14	e	None	500	415-550	44.0	0	None
Total					2,522		76.4

[a]Runs are listed in chronological order.

[b]High temperature reached during removal of high-ZrF_4-content salt to waste.

[c]High temperature resulted from attempts to melt a salt plug in the salt-transfer line.

[d]Failure of two temperature controllers resulted in the lower part of the fluorinator being heated to 890°C for a short time prior to fluorination.

[e]Salt was blended from 27.5-27.5-45 and 37.5-37.5-25 mole % NaF-LiF-ZrF_4 salts. No samples were taken.

Table 8. Fluorinator Decontamination History

Cleaned After Run:	Cleaning Solution Used[a,b]	Time (hr)	Temperature (°C)
TU-7 (14 runs)	0.35 M ammonium oxalate	4 4	60 95
TU-11 (21 runs)	No cleaning done		
T-11 (29 runs)	0.35 M ammonium oxalate (6 washes)	307 142	50-95 25
	0.3 M $Al(NO_3)_3$	70	50-95
	0.1 M $Al(NO_3)_3$	20 52	50-95 25
	0.1 M $Al(NO_3)_3$-0.01 M HNO_3 (2 washes)	86 25	50-95 25
	5-1-1 wt % NaOH-H_2O_2-sodium tartrate	10	25
	5-2-2 wt % NaOH-H_2O_2-sodium tartrate	20	25
T-14 (40 runs)	0.3 M ammonium oxalate (7 washes, circulated) (1 wash, static)	300 103 92.5	25-80 80-95 25
	Detergent solution[c] (2 washes)	3 18	25-80 80-95
	5-1-1 wt % NaOH, H_2O_2, sodium tartrate	20	25

[a]The top half of the fluorinator was not exposed to cleaning solution during some washes.

[b]Water rinses are not included.

[c]Approximately 1.25 lb of dishwasher detergent in 350 gal of water.

the neck section was at about 425, and the upper section was at about 375. Temperatures were kept at fairly constant values throughout each run. Salt from the hydrofluorinator (about 27.5-27.5-45 mole % $NaF-LiF-ZrF_4$ plus uranium, mp about 450°C) was transferred to the bottom section, filling it to 3 to 14 in. below the 5-3/4-in.-diam section.

The salt was sparged with nitrogen at about 14 std liters/min (slm) for 20 min to ensure a uniform mixture for sampling. Salt samples were taken by lowering a ladle on a chain through the 1-in. pipe extending into the upper section of the fluorinator. During the sampling period, an attempt was made to prevent air entry into the vessel by balancing the pressure in the vessel against that in the sample cubicle with nitrogen purges. However, there was some air flow into the fluorinator, particularly in the runs prior to run T-11.

After sampling, the salt was fluorinated until the uranium content was less than 10 ppm. This was usually done in two steps. Fluorine[a] was first introduced at about 6 slm for 1 hr and 40 min and then at about 13 slm for 20 min.[b] After fluorination, the vessel was immediately purged with nitrogen and the salt resampled. The salt then remained in the vessel for several hours while the UF_6 was desorbed from the movable-bed absorber (filled with NaF pellets). Fluorine was used to sweep the UF_6 from the NaF; consequently there was some exposure of the upper portion of the fluorinator to a fluorine-nitrogen atmosphere during that time, but only the exposure during fluorination and conditioning was included in

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[a]Typical F_2 analysis is given in Table 2A in the Appendix.

[b]Additional fluorination was done if required to reduce the uranium content of the salt to less than 10 ppm.

corrosion-rate determinations. After desorption of the UF_6, a portion of the NaF pellets from the absorber was discharged into the fluorinator. The salt was again sparged with nitrogen and sampled. Finally, the fluorinator was emptied and then cooled to room temperature in a nitrogen atmosphere. Typical fluorinator operating conditions for runs during zirconium processing are given in Table 9.

Table 9. Typical Fluorinator Operation Conditions for Each Run During Zirconium Processing

Fluorinator Condition	Typical Time Required per Run (hr)
Heat up to 500°C (no salt except heel)	2
At 500°C with no salt present	2
At 500°C with salt but no F_2	50
At 500°C with salt and F_2	2
At 500°C with F_2-N_2 mixture in top section	4
Cool down from 500°C to 100°C with no salt present	36

Operating History of Fluorinator

The fluorinator and associated lines were installed new at the beginning of the zirconium program and were used throughout the program with only a few changes. These changes, along with abnormal operating conditions that might have influenced corrosion, are given in this section.

The movable-bed absorber was installed above the fluorinator at the end of T-7 (7 runs). Prior to that time, fixed-bed NaF absorbers filled with NaF pellets were used. The absorber was attached to the 5-in.-diam pipe above the fluorinator; flanges and a copper O-ring gasket were used.

During the first R-series runs, this flanged connection developed a leak, and, after T-11, it was replaced with a welded connection. The leak was apparently caused by overheating the copper O-ring gasket. Only one other leak occurred in the fluorinator, and it developed prior to run TU-13 in the welded joint between the sampling line and the fluorinator. It apparently was caused by the vibrator used on the line during sampling. The weld was repaired, and the sampling procedures were modified to reduce the use of the vibrator, preventing further leaks.

In other piping changes, the salt-sampling line was changed from 3/4-in. to 1-in. sched-40 pipe after T-7 (7 runs) in order to make passage of the ladle through the line easier. The waste salt line from the fluorinator to the waste can was replaced after TU-7 (14 runs) because the line had been bent when the fluorinator was forced out of alignment by the furnace.

Overheating of the lower section of the fluorinator occurred during runs T-8, T-9 and R-8. A high-melting salt was charged to the system during T-8, and the fluorinator was heated to 750°C to prevent freezing. During T-9, a plug formed in the salt-transfer line between the hydrofluorinator and fluorinator, and the temperature was increased to about 715°C to try to melt the plug. A section of the transfer line was replaced during this run, and the entire line was replaced after T-10. During R-8 simultaneous failure of two temperature controllers resulted in the lower section of the fluorinator being heated to about 890°C for a short time, but the overheating apparently was not detrimental.

Six groups of 1/4-in.-diam corrosion rods were exposed to the fluorinator environment during the zirconium program. These specimens were made

of Nickel 201 rod welded with filler metal 61 and of other metals that were promising for fluorinator construction. The runs during which each group of rods was exposed are given in Table 10.

Table 10. Corrosion-Rod Exposure in the Fluorinator During Zirconium Processing

Corrosion Rod Group Number	Runs
I	T-1 through T-7
II	TU-1 through TU-5
III	TU-6 and TU-7
IV	T-8 through TU-10
V	TU-11 through T-11
VI	TU-13 to present[a]

[a]Rods were still in the fluorinator at the end of the zirconium program (T-14).

Two 4-in.-diam disks were trepanned from the lower section of the fluorinator after T-11 (29 runs) for metallurgical analysis. They were removed from the intersection of girth and seam welds (Fig. 10) after radiography revealed that the weld had been selectively attacked. New plugs were welded into the holes from which the disks were removed.

Fluorinator Corrosion Measurements and Results

Bulk Metal Losses

Bulk metal losses from the fluorinator were determined primarily by Vidigage wall-thickness measurements. These measurements gave the predominant thickness and did not include pits or intergranular corrosion, which were measured by other methods. An extensive survey of the fluorinator

was made after TU-7 (14 runs).[3] A vertical row of measurements was made in each quadrant of the vessel, with thickness being determined at 1-in. intervals. These thicknesses were then compared with the original wall thickness to determine losses.

The maximum wall-thickness loss of 27 mils (0.9 mil/hr of fluorine exposure) occurred in the 5-3/4-in.-diam neck. This corrosion rate was consistent with rates previously obtained for the Mark I and II fluorinators.[21] The maximum loss in the lower section after TU-7 was 16 mils (0.52 mil/hr of fluorine exposure), and the maximum loss in the upper de-entrainment section was 14 mils (0.5 mil/hr of fluorine exposure).

A limited number of Vidigage measurements was made, in the lower section only, after runs TU-11 (21 runs)[4] and T-11 (29 runs). Measurements were not made in the upper section because it was covered with insulation. The lower-section measurements were made at 3-in. intervals in one vertical line. A comparison of the wall-thickness losses in the lower section at various times during the program is given in Table 11 below. The lower total-wall-thickness losses measured after 21 and 29 runs evidently resulted from the small number of readings taken then, compared with the extensive survey made after 14 runs. However, the measurements made after 21 and 29 runs indicate that no extensive wall-thickness loss occurred during that time.

Additional corrosion information for the fluorinator was obtained after T-11 (29 runs) from two 4-in.-diam disks trepanned from the lower section.[9] They were removed for metallurgical examination after gamma radiography revealed that welds in the vessel had been selectively attacked. Micrometer measurements of the base metal (corrosion of the

Table 11. Bulk Metal Losses in the Bottom 16-in.-diam Section of the Fluorinator During Zirconium Processing

Number of Runs	Wall Thickness Loss (mils)		Corrosion Rate (mils/hr of fluorine exposure)	
	Maximum	Average	Maximum	Average
14[a] (after TU-7)	16	6	0.52	0.19
21[b] (after TU-11)	9	4.7	0.23	0.12
29[b] (after T-11)	9	5	0.15	0.09

[a]Measurements made at 1-in. intervals in 4 quadrants.

[b]Measurements made at 3-in. intervals in 1 quadrant.

weld metal will be discussed later) indicated wall-thickness losses of 2 to 10 mils (0.04 to 0.17 mil/hr of fluorine exposure) for the upper disk and 5 to 15 mils (0.09 to 0.26 mil/hr of fluorine exposure) for the lower one.[a] Wall-thickness measurements made during the zirconium program are given in Table 12.

The disks trepanned from the fluorinator after T-11 provided access holes through which the internal piping was measured. The 2-in.-diam draft tube had a diameter decrease of about 30 mils (15 mils surface loss). All 1/2-in.-diam piping had decreased 0 to 25 mils, with the upper portion measuring about 10 mils more than the bottom.

Corrosion rods exposed to the fluorinator environment during the first 29 runs[b] also provided bulk-metal-loss data. Rods made of sections

[a]There was an 8- to 10-mil variation in the original wall thickness at locations from which the disks were removed.

[b]Five groups (of six rods each) were exposed during the first 29 runs. A sixth group of rods was installed at the end of 29 runs but was not removed at the end of the zirconium program (40 runs).

Table 12. Bulk Metal Losses from the Nickel 201 Fluorinator During Zirconium Processing

Section of the Fluorinator Measured	Number of Runs	Fluorine[a] Exposure Time (hr)	Molten Salt Exposure Time (hr)	Total Wall Thickness Loss (mils)		Corrosion Rate (mils/hr of F_2)		Corrosion Rate (mils/month of molten-salt exposure)	
				Maximum	Average	Maximum	Average	Maximum	Average
Bottom 16-in.-diam section[c]	29	57.6	1,922	9	5	0.15	0.09	3.4	1.9
4-in.-diam disk trepanned from top of lower section	29	57.6	1,922	2 to 10[b]	—	0.04 to 0.17	—	0.8 to 3.6	—
4-in.-diam disk trepanned from the bottom of the lower section	29	57.6	1,922	5 to 15[b]	—	0.09 to 0.26	—	1.9 to 5.7	—
Bottom 16-in.-diam section[c]	21	38.7	1,337	9	4.7	0.23	0.12	4.9	2.6
Bottom cone[c]	21	38.7	1,337	14	10.0	0.4	0.3	7.7	5.5
Bottom 16-in.-diam section[d]	14	30.9	694	16	6	0.52	0.19	16.9	6.3
Bottom cone[d]	14	30.9	694	13	6	0.4	0.2	13.7	6.3
Bottom head[d]	14	30.9	694	22	9	0.7	0.3	23.2	9.5
Neck[d]	14	30.9	694	27	13	0.9	0.4	28.4	13.7
Top cone[d]	14	30.9	694	20	7	0.6	0.2	21.1	7.4
Top 16-in.-diam section[d]	14	30.9	694	14	4.5	0.5	0.1	14.7	4.7
Top head[d]	14	30.9	694	10	4	0.3	0.1	10.5	4.2

[a]Fluorine exposure time does not include vessel exposure during desorption.

[b]Based on original thickness of 0.370 to 0.378 at top and 0.370 to 0.380 at bottom.

[c]Only one set of measurements were made vertically every 3 in.

[d]Measurements were taken every inch in each quadrant.

of Nickel 201, some of which were joined with weld filler metal 61, were included in each of the five groups used during the first 29 runs. The rods were inserted in the lower section of the fluorinator. Separate measurements were made for both the Nickel 201 and weld filler metal 61 in the salt, interface, and vapor regions of the rod. The runs during which each group of rods was exposed is given in Table 10. Table 13 is a summary of the bulk metal losses. Corrosion rates for both the Nickel 201 rods and the weld filler metal 61 varied widely among the groups.[6,9,22] The bulk-metal loss rate for the Nickel 201 was from 0.06 to 2.5 mils/hr of fluorine exposure. The maximum rate for the weld filler metal was from 0.09 to 3.7 mils/hr of fluorine exposure. In general, bulk-metal losses were highest at the interface and lowest in the vapor region for both the Nickel 201 and weld filler metal 61 rods. Weld filler metal 61 had a slightly higher loss than the Nickel 201.

It is difficult to relate the wide variations in bulk-metal loss in various sets of corrosion rods to operation conditions or the use of decontamination solutions. However, unusually high rates (over 1 mil/hr of fluorine exposure) occurred only in the group-III rods, which were exposed for two nonradioactive runs plus an ammonium oxalate wash. While these runs were essentially identical with later runs, the later runs were generally smoother because of refinements made in operating techniques.

Fluorinator Pitting

The pitting attack on the fluorinator wall was measured after TU-7 (14 runs) by gamma radiography.[3] Pits up to 10 mils deep were found in the upper section and in the conical section. No further measurements were made since that time. However, after T-11 (29 runs), the fluorinator

Table 13. Bulk-Metal Loss Rates for Nickel 201 and Weld Filler Metal 61 Corrosion Rods (Groups I through V) in the Fluorinator

Material	Group Number	Fluorine Exposure (hr)	Molten Salt Exposure (hr)	Corrosion rate (mils/hr of F_2 Exposure)					
				Vapor		Interface		Salt	
				Maximum	Average	Maximum	Average	Maximum	Average
Nickel 201[a]	I	12	367	0.06	0.04	0.08	0.07	0.09	0.06
Nickel 201[a]	II	10.5	205.5	0.14	0.08	0.43	0.40	0.34	0.28
Nickel 201	II	10.5	205.5	0.13	0.11	0.54	0.42	0.34	0.30
Nickel 201[a]	III	3.1	99	0.21	0.20	2.1	1.9	2.0	1.5
Nickel 201	III	3.1	99	0.45	0.34	2.5	2.1	1.7	1.5
Nickel 201	IV	5.8	601	0.26	0.12	0.24	0.21	0.93	0.38
Nickel 201	IV	5.8	601	0.33	0.18	0.36	0.30	0.48	0.39
Nickel 201	V	20.9	625	—	—	—	—	0.18	0.13
Average					0.15		0.77		0.57
Weld filler metal 61[a,b]	I	12	367	0.11	0.06	0.09	0.08	0.10	0.08
Weld filler metal 61[a,b]	II	10.5	205.5	0.26	0.23	0.58	0.57	0.64	0.59
Weld filler metal 61[b]	II	10.5	205.5	0.19	0.09	0.64	0.57	0.35	0.34
Weld filler metal 61[a,b]	III	3.1	99	1.17	1.3	3.7	3.0	2.5	2.4
Weld filler metal 61[b]	III	3.1	99	0.54	0.29	3.2	2.8	2.3	2.0
Weld filler metal 61[b]	IV	5.8	601	0.33	0.22	0.35	0.30	0.29	0.26
Average					0.37		1.22		0.95

[a]These corrosion rods were fluorine-conditioned before being installed in the fluorinator.

[b]Rates are for weld filler metal 61 used in joining sections of the corrosion rods.

was inspected visually, and no unusual corrosive attack on the Nickel 201 metal was observed.

Intergranular Corrosion

Nickel 201 corroded intergranularly in the fluorinator atmosphere (Fig. 11). This intergranular attack was visible in as-polished metallurgical specimens, and, when the specimens were etched with 1:1 nitric-glacial acetic acids, additional grain-boundary modification became evident. In this report, intergranular corrosion, grain-boundary modification, and a small amount of surface roughness have been classified as penetration determined by metallography.

Intergranular corrosion and grain-boundary modification represented a significant part of the total corrosive attack on the Nickel 201, as shown by corrosion-rod data in Table 14 and by the fluorinator-specimen data in Table 15. The weld filler metal 61, on the other hand, showed much less grain-boundary modification than bulk metal loss.

The two 4-in.-diam disks trepanned from the fluorinator after T-11 (29 runs) probably give the most reliable corrosion data obtained for the lower section of the fluorinator. The lower disk was taken from near the bottom of the lower section in a location that would have been submerged in salt during operation. The upper one was removed from an area slightly above the normal salt interface. Corrosion data are given in Table 15. Note that in addition to the corrosive attack inside the vessel, grain-boundary modification occurred on the outside as a result of air oxidation.

Fluorinator Corrosion by Aqueous Cleaning Solutions

The fluorinator was periodically cleaned with aqueous solutions to reduce the radiation level and to expose the surface for examination

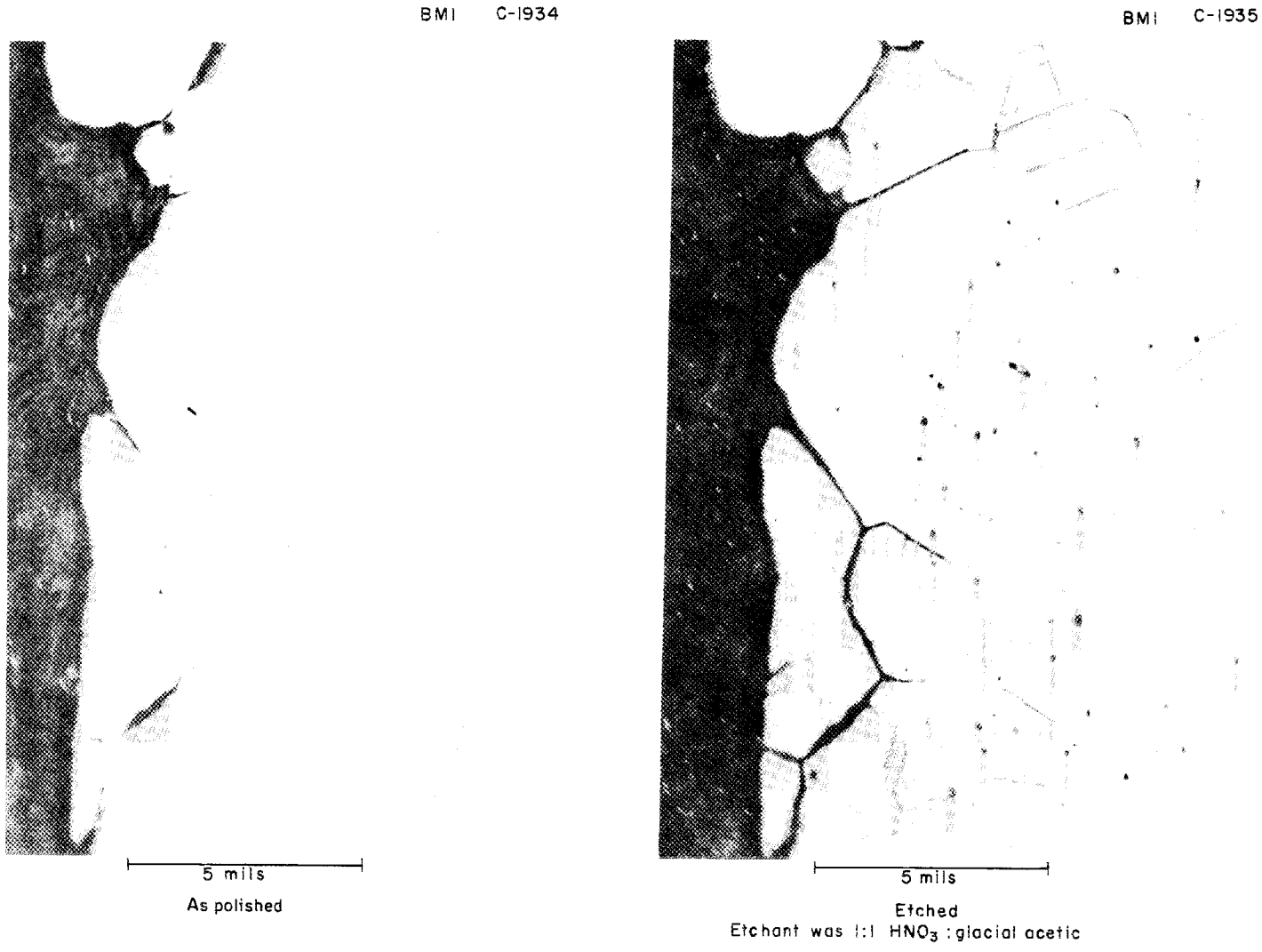

Fig. 11. Grain-Boundary Modification of Nickel 201 Specimens Removed From the Fluorinator Wall After Twenty-nine Runs.

Table 14. Maximum Corrosion Rates for Nickel 201 and Weld Filler Metal 61 in Groups I Through V Fluorinator Corrosion Rods

Group No.	Vapor				Interface				Salt			
	Bulk Metal Loss (mils)	Metal lurgical[a] Loss (mils)	Total Corrosion (mils)	Total Corrosion (mils/hr F_2)	Bulk Metal Loss (mils)	Metal lurgical[a] Loss (mils)	Total Corrosion (mils)	Total Corrosion (mils/hr F_2)[d]	Bulk Metal Loss (mils)	Metal lurgical[a] Loss (mils)	Total Corrosion (mils)	Total Corrosion (mils/hr F_2)[d]
Nickel 201												
I[b]	0.7	1.5	2.2	0.2	1.0	9.5	10.5	0.9	1.1	11.5	12.6	1.1
II[b]	1.5	5.5	7.0	0.7	4.6	5.5	10.1	1.0	3.6	7.0	10.6	1.0
II	1.4	6.0	7.4	0.7	5.7	4.5	10.2	1.0	3.6	7.0	10.6	1.0
III[c]	0.7	2.0	2.7	0.9	6.5	2.5	9.0	2.9	6.1	2.7	8.8	2.9
III	1.4	2.5	3.9	1.3	7.8	5.0	12.8	4.1	5.1	6.0	11.1	3.6
IV	1.5	7.0	8.5	1.5	1.4	10.0	11.4	2.0	5.4	31.0	36.4	6.2
IV	1.9	6.0	7.9	1.4	2.1	12.0	14.1	2.5	2.8	7.0	9.8	1.7
V	—	—	—	—	—	—	—	—	3.7	3.0	6.7	0.32
Weld filler metal 61												
I[b]	1.3	0	1.3	0.1	1.1	0.2	1.3	0.1	1.2	2.0	3.2	0.3
II[b]	2.7	1.0	3.7	0.4	6.1	0.5	6.6	0.6	6.7	0	6.7	0.6
II	2.0	0.2	2.2	0.2	6.8	0	6.8	0.6	3.7	0	3.7	0.4
III[c]	5.3	0	5.3	1.7	11.5	0	11.5	3.7	7.8	0	7.8	2.5
III	1.7	1.0	2.7	0.9	9.9	2.5	12.4	4.0	7.2	2.5	9.7	3.1
IV	1.9	0.5	2.4	0.4	2.0	1.5	3.5	0.6	1.7	2.5	4.2	0.7

[a]The metallurgical loss includes both intergranular attack and grain-boundary modification.

[b]Control specimen - fluorine conditioned for 5.3 hr at 560-670°C.

[c]Control specimen - fluorine conditioned for 3.2 hr at 600-645°C.

[d]Corrosion rate is in mils per hr of fluorine exposure.

Table 15. Corrosion of Nickel 201 Specimens Removed from the Fluorinator Wall After 29 Runs

Location	Bulk Metal Loss (mils)	Grain Boundary Mod. Inside Surface (mils)	Grain Boundary Mod. Outside Surface (mils)	Total Attack (mils)	Corrosion Rate (mils/hr of F_2)	Sound Metal Remaining (mils)
Upper trepanned section	2 to 10[a]	5	9	16 to 24	0.28 to 0.42	354
Lower trepanned section	5 to 15[a]	6	11	22 to 32	0.38 to 0.56	348

[a]Based on an 8- to 10-mil variation in the original wall thickness.

(Table 8). Ammonium oxalate solutions (0.35 M) were used for removing salt films, aluminum nitrate (0.1 M)—nitric acid (0.01 M) solution was used after T-11 (29 runs) as a mild corrodent to remove radioactive material that had penetrated into the areas left by intergranular corrosion of the Nickel 201, and sodium hydroxide-hydrogen peroxide-sodium tartrate solution (5-1-1 to 5-2-2 wt %) was used to remove back-adsorbed activity.

Corrosion of ammonium oxalate solution on nickel had previously been determined to be low.[8,9] Nickel corrosion rates for 0.5 M ammonium oxalate at reflux temperature were 0.064 to 1.22 mils/month, depending on pH and salt content.[23] When the aluminum nitrate-nitric acid and caustic-peroxide-tartrate solutions were circulated through the fluorinator, the nickel content was watched carefully to prevent excessive corrosion.[a]

[a]Assuming uniform corrosion, the nickel analyses indicated an average wall-thickness loss of 1.7 mils in the lower 16-in. section of the fluorinator due to the aqueous cleaning after T-11. Most of the corrosion occurred during the use of the $Al(NO_3)_3$-HNO_3 solutions.

However, an examination of the fluorinator after the cleaning following run T-11 (29 runs) revealed that the weld filler metal 61 had been selectively attacked. This attack on a specimen cut from the fluorinator is shown in Fig. 12. The weld metal was removed to a depth of about 40 mils, but, as shown in Fig. 12, the thickness of the remaining weld metal was still about the same as that of the vessel wall. Weld metal loss was fairly uniform throughout the vessel, and gamma radiography of the welds in the lower section indicated that there were no areas of extensive penetration.

Studies were made at BMI[9] and ORNL[8] to determine the cause of the selective attack on weld filler metal 61. At BMI, corrosion specimens made from the fluorinator wall, as well as prepared specimens, were exposed to alternating cycles of boiling 0.1 M $Al(NO_3)_3$—0.01 M HNO_3 and 5-2-2 wt % NaOH- H_2O_2-$NaC_2H_4O_6$ at room temperature. The results of this exposure, given in Table 16, indicate that the $Al(NO_3)_3$-HNO_3 is more corrosive to both Nickel 201 and weld filler metal 61 than is the caustic-peroxide-tartrate. Initial corrosion rates in the $Al(NO_3)_3$-HNO_3 during the first 3 hr were considerably higher than later rates. The use of caustic-peroxide-tartrate appears to increase corrosion by subsequent treatment with $Al(NO_3)_3$-HNO_3. Neither the prepared corrosion specimen of Nickel 201 welded with filler metal 61 nor the filler metal 61 corrosion specimens indicated selective attack by the decontaminating solution. However, the weld filler metal 61 specimen removed from the fluorinator was selectively attacked, as shown in Fig. 13. Based on these studies, it was concluded that the weld filler metal 61 attack was caused by the aluminum nitrate-nitric acid cleaning solution used after run T-11.

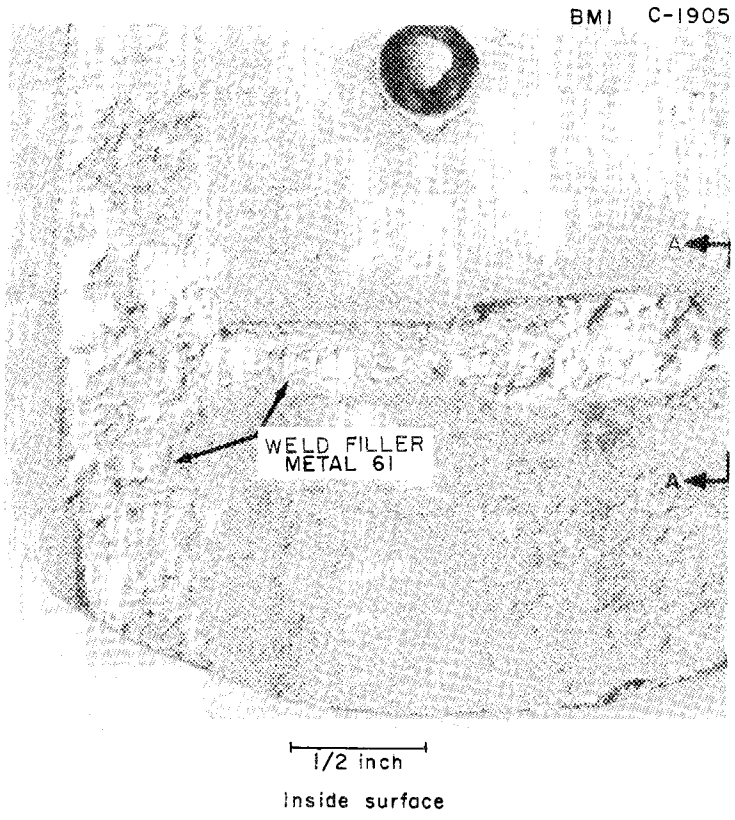

Fig. 12. Section of the Fluorinator Wall Showing Corrosion of the Weld Filler Metal 61 After Twenty-nine Runs and 3 Aqueous Cleanings.

Table 16. Corrosion Rate of Fluorinator Materials in Alternating Cycles of Boiling 0.01 N HNO_3—0.1 N $Al(NO_3)_3$ and 5-2-2-wt % NaOH- H_2O_2-$NaC_2H_4O_6$ at Room Temperature

Exposure Conditions	Corrosion Rate		
	Nickel 201[a] Fluorinator Specimens (mils/month)	Nickel 201[a] Test Specimens (mils/month)	Weld Filler Metal 61 Rod (mils/month)
$Al(NO_3)_3$-HNO_3 - first 3 hr	152 to 244	108 to 166	59 to 67
$Al(NO_3)_3$-HNO_3 - next 81 hr	34 to 36	11 to 23	14
Caustic-peroxide-tartrate - next 20 hr	6 to 8	3 to 6	7 to 8
$Al(NO_3)_3$-HNO_3 - next 16 hr	60 to 67	57 to 63	39 to 41
Caustic-peroxide-tartrate - next 20 hr	4 to 5	2 to 4	4 to 5
$Al(NO_3)_3$-HNO_3 - next 20 hr	78 to 87	47 to 53	36 to 41
Cumulative rate for 120 hr of $Al(NO_3)_3$-HNO_3 and 40 hr of caustic-peroxide-tartrate	39 to 40	22 to 28	18.7

[a]Specimens had weld filler metal 61 in seam welds.

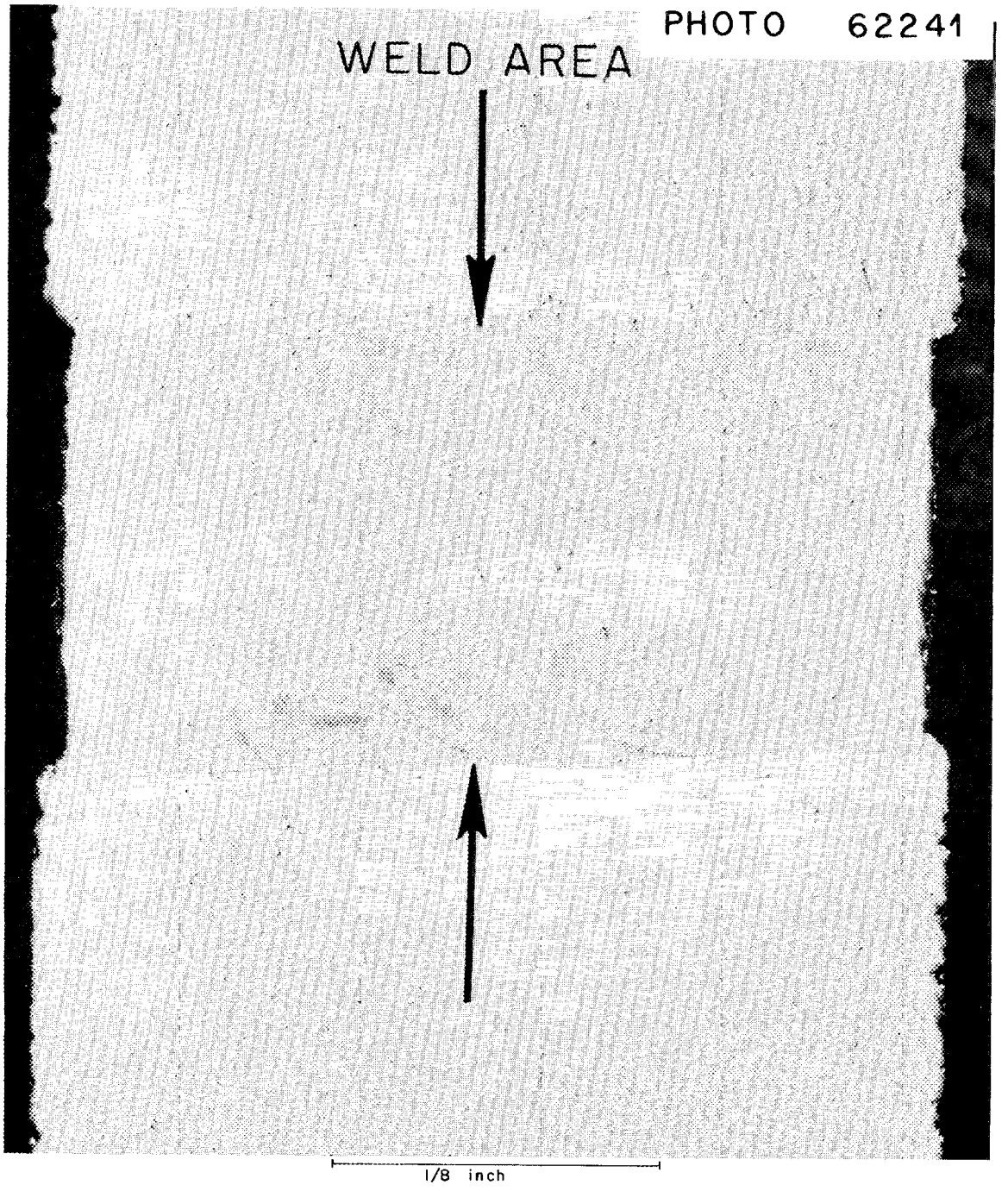

Fig. 13. Selective Corrosion of Weld Filler Metal 61 by Aqueous Cleaning Solutions. Vertical faces were flat before exposure to solutions.

The reason is not known for the difference between the corrosion rate for the weld filler metal 61 from the fluorinator specimen and that for the prepared specimens (which did not show selective attack of the weld filler metal 61). Analyses of the fluorinator welds gave a typical weld filler metal 61 composition. The larger ratio of Nickel 201 to weld filler metal 61 in the fluorinator, compared with that for the corrosion specimen, may have increased the weld filler metal 61 attack in the fluorinator by galvanic corrosion.[8]

Air Oxidation of Nickel 201

Specimens removed from the lower portion of the fluorinator after run T-11 (29 runs) showed that grain-boundary modification had occurred on the exterior surface to a depth of 9 mils and 11 mils on the upper and lower specimens, respectively (Table 15). The residence time of molten salt in the vessel provides a conservative estimate of the time that the exterior of the vessel was heated. Based on salt-residence time, the exterior corrosion rate was 3.4 and 4.2 mils/month. Studies at BMI gave a corrosion rate of 1.6 mils/month for Nickel 201 in air at 700°C for 2000 hr.[7] In these studies, the nickel scale was adherent, but there was considerable intergranular corrosion.

The Mark I and II Nickel 201 fluorinators used in previous Volatility Pilot Plant programs exhibited similar exterior corrosion loss.[21] The Mark I vessel had a 3- to 8-mil corrosion loss (1.8 to 4.7 mils/month of exposure to molten salt) after 1250 hr of molten salt at 600 to 725°C. The Mark II vessel was exposed for 1950 hr to molten salt at 540 to 730°C and showed an exterior corrosion loss of 1 to 6 mils (0.37 to 2.2 mils/month of exposure to molten salt).

Corrosion of Other Metals in the Fluorinator Environment

Corrosion-rod studies in the fluorinator environment included metals potentially suitable for fluorinator construction. The specimens included binaries of nickel and iron, cobalt, aluminum, magnesium, and molybdenum, and specimens made of INOR-8, INOR-1,[a] HyMu 80,[b] Nickel 201, weld filler metal 61, INCO-41,[c] E-nickel[d] and high-purity vacuum-melted (HPVM) nickel. Nickel 201 specimens were included in each of the five groups of rods evaluated during the zirconium program. The other metals were included in one or more of the groups.

The specimens were located in the lower section of the fluorinator, and portions of them were exposed to vapor, interface, and salt regions. Maximum corrosion rates for specimens in each group and the location in which maximum corrosion occurred are given in Table 17. The runs during which each groups was exposed and the run conditions are given in Tables 10 and 7. Groups II, III, and IV were exposed to normal fluorinator conditions. Group I was exposed to salt containing no uranium; consequently, the salt was not fluorinated. Group V was exposed to normal fluorinator conditions plus the extensive aqueous cleaning given the system after T-11. The aqueous cleaning is responsible for a large part of the corrosion of this group, particularly that of the HyMU 80 specimens.

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[a] INOR-1 nominal composition (wt %) - Ni, 78; Mo,20; Fe,0.3; Mn,0.5; Si,0.5.

[b] HyMu 80 nominal composition (wt %) - Ni,79; Mo,4.0; Mn,0.50; Si, 0.15; Fe,bal.

[c] INCO-41 (Ni filler metal) nominal composition (wt %) - Ni, 97 min; Cu,0.25; Mn,0.35; Fe,0.4; Si,1.0; Ti,0.5 max.

[d] E-nickel nominal composition (wt %) - Ni-2Mn.

Table 17. Maximum Corrosion Rates for Groups I Through V, Fluorinator Corrosion Rods[12]

Group No.	Metal	Location of maximum corrosion[a]	Corrosion Rate (mils per hr of F_2 exposure) Metal Loss[b]	IG[c]	Total[d]
I	L-nickel, conditioned	L	0.09	0.96	1.1
	Weld filler metal 61, conditioned	L	0.10	0.17	0.27
	Nickel HPVM	L	0.06	10.4	10.5
	E-nickel	L	0.07	0.29	0.36
	Ni-5 Fe	L	0.09	0.06	0.15
	Ni-10 Fe	V	0.08	0.83	0.91
	Ni-20 Fe	L	0.08	0.42	0.50
II	L-nickel, conditioned	L	0.34	0.67	1.0
	Weld filler metal 61	L	0.64	0	0.64
	L-nickel	L	0.34	0.67	1.0
	Ni-5 Co	L	0.57	3.71	4.28
	Weld filler metal 61	IF	0.65	0	0.65
	Ni-10 Co	IF	0.78	0.33	1.11
	Ni-1 Al	IF	0.55	0	0.55
	Ni-3 Al	IF	0.82	1.48	2.29
III	L-nickel, conditioned	L	2.0	0.9	2.9
	Weld filler metal 61, conditioned	IF	3.7	0	3.7
	L-nickel	IF	2.5	1.6	4.1
	Weld filler metal 61	IF	3.2	0.8	4.0
	Ni-1 Mg	IF	2.8	0	2.8
	Ni-0.1 Mg	IF	3.3	0	3.3
	Ni-0.05 Mg	IF	2.9	0	2.9
	HyMu 80	IF	1.3	0	1.3
IV	L-nickel	L	0.9	5.3	6.2
	Weld filler metal 61	L	0.3	0.4	0.7
	L-nickel	IF	0.4	2.1	2.5
	INCO-41	L	0.6	0.9	1.5
	Ni-10 Fe	L	1.3	0.7	2.0
	HyMu 80	L	1.2	0.4	1.6
	INOR-8	L	1.0	0	1.0
V	L-nickel	L	0.18	0.14	0.32
	Ni-1 Al	L	1.83	0	1.83
	Ni-5 Mo	L	0.99	0	0.99
	INOR-1	L	1.31	0	1.31
	INOR-8	V	0.53	0	0.53
	HyMu 80	L	2.62	0	2.62

[a] V = vapor; L = liquid; IF = vapor-liquid interface.

[b] By micrometer readings.

[c] Intergranular attack and grain boundary modification.

[d] Based on sound metal remaining, assuming that intergranularly attacked and leached portion is unsound.

Corrosion rates of Nickel 201 and other materials present in more than one group showed considerable variation between groups. This variation has not been fully explained, although it may have been due to differences in the HF and sulfur content of the fluorinator salt.

Although there was a considerable variation in corrosion rates of alloys from different groups, several conclusions are apparent from the corrosion rod results. The bulk metal loss from the nickel binary alloys was about the same as for Nickel 201, but, the presence of iron, aluminum, and manganese considerably reduced the intergranular corrosion. Extra-high-purity nickel was most susceptible to both bulk metal loss and intergranular attack. Materials that show promise of improved performance over Nickel 201 for fluorinator construction were weld filler metal 61, E-nickel, Ni-5 Fe, Ni-1Al, INOR-8 and HyMu 80. A more complete coverage of the corrosion rod data can be obtained from refs. 6, 9, 12 and 22.

DISCUSSION AND CONCLUSIONS

The corrosion data obtained from the hydrofluorinator during 40 zirconium processing runs indicates that INOR-8 is a suitable structural material if a corrosion allowance is included in the design of the vessel. Cracking in the lower section of the vessel, which caused the most concern in the present hydrofluorinator, is thought to be due to the use of a substandard piece of INOR-8 and is therefore not expected to be a problem in future hydrofluorinators.

The maximum bulk metal loss in the hydrofluorinator, 0.14 mil/hr of HF exposure (38 mils/month of molten salt), was measured in the replacement bottom used for the last 11 runs. However, this high rate is questionable because of the accuracy of the measuring device and the large

variation in the original wall thickness of the replacement bottom. Also, there is some indication both in this vessel and in previous hydrofluorinators[24] that the corrosion rate decreases after the first few runs. The maximum rate in the remainder of the vessel after 40 runs was 0.028 mil/hr of exposure to HF (8.1 mils/month of exposure to molten salt).

The maximum pitting attack measured in the hydrofluorinator was 10 mils after 14 runs and 20 mils after 40 runs. While these limited data are not sufficient to determine the rate of pit growth, a value of 0.5 mil/run appears reasonable for estimating the life expectancy of the vessel.

Based on the maximum rate of 0.14 mil/hr of HF exposure, the bulk metal loss during a normal run (24 hr of exposure) would be 3.1 mils. The assumption that a pitting attack of 0.5 mil/run occurred at the same location as the maximum bulk metal loss would give a total loss of 3.6 mils/run. The hydrofluorinator was constructed with a 125-mil corrosion allowance, of which about 100 mils still remain. Therefore the hydrofluorinator should be suitable for at least 28 more runs. According to the loss rate for bulk metal, 0.028 mil/hr of exposure to HF, which was the maximum observed in the original vessel after 40 runs, the estimated life would be 85 additional runs.

Corrosion results from the Mark III fluorinator during zirconium fuel processing appear to be consistent with previous results from the Mark I and Mark II fluorinators.[21] All three were made of Nickel 201; however, the Mark I and Mark II fluorinators were operated in the 540-to-730°C temperature range and with an $NaF-ZrF_4$ salt containing about 11 wt % UF_4, while the Mark III fluorinator was operated at about 500°C with an $NaF-LiF-ZrF_4$ salt containing less than 1 wt % UF_4. The maximum corrosion

rates observed in the Mark I and Mark II fluorinators, including internal and external intergranular corrosion, was 1.2 and 1.1 mils/hr of F_2 exposure, respectively. The maximum rate occurred in the vapor section in the Mark I vessel and in the salt-containing region in the Mark II.

The maximum corrosion rate observed for the Nickel 201 in the Mark III fluorinator was 0.9 mil/hr of F_2 in the vapor region. This rate was based on wall-thickness measurements made after the first 14 runs and represents only bulk metal loss since there has been no metallurgical examination of the metal in the vapor region of the vessel. Specimens removed from the lower fluorinator wall (the salt-containing region) after 29 runs had a maximum corrosion rate of 0.56 mil/hr of F_2, including internal and external intergranular attack. Pitting up to 10 mils deep was observed in the vapor section of the fluorinator after 14 runs.

The selective corrosion of weld filler metal 61 observed after 29 runs was due primarily to the nitric acid-aluminum nitrate solution used for cleaning the system. Its use for fluorinator cleaning has been discontinued. Corrosion-rod data indicate that while weld filler metal 61 has a higher bulk metal loss rate than Nickel 201 in the normal fluorinator environment it has a lower total corrosion rate because of the low rate of intergranular attack. It is therefore felt that corrosion of weld filler metal 61 will not be the limiting factor in the life of the fluorinator.

Additional corrosion data would be required from the vapor region of the Mark III fluorinator in order to determine the maximum total corrosion rate of the vessel; however, a rate of 1.2 mils/hr of F_2 exposure appears to be a reasonable estimate, based on past experience and on the maximum

bulk metal loss measured after 14 runs, 0.9 mil/hr of F_2 exposure. The Mark III fluorinator was built with a corrosion allowance of 175 mils. So far, it has been exposed to 76.4 hr of F_2 attack, and, at an estimated maximum corrosion rate of 1.2 mil/hr of F_2, there would be about 83 mils of corrosion allowance remaining after the 40-run zirconium program. Based on a 2-hr fluorine sparge per run (corrosion rate, 2.4 mils/run), the estimated life of the fluorinator would be 34 additional runs. Based on the fluorine-induced corrosion obtained from specimens cut from the lower fluorinator wall after 29 runs, 0.56 mil/hr of F_2 exposure, the estimated life of the vessel would be 117 additional runs.

Future corrosion information is expected to be obtained from continued periodic examinations of the hydrofluorinator and fluorinator vessels and from metallurgical examinations when they are removed from the process at the end of their useful life.

Data obtained from corrosion rods and from laboratory studies at BMI and ORNL[7,25,26,27,28] indicate that INOR-8 and HyMu-80 show promise of improved performance over Nickel 201 for future fluorinator construction.

ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance given by the Inspection Engineering Department, which made wall-thickness measurements and radiographs of the vessels, and the Analytical Chemistry Division, which performed many chemical analyses.

Special credit is due personnel of the Corrosion Division, Battelle Memorial Institute and the ORNL Metals and Ceramics Division for performing a large part of the metallurgical examinations and corrosion evaluations, and to Chemical Development B for their assistance in many of the corrosion problems.

The authors also wish to thank W. H. Carr and Sydney Mann for their helpful suggestions in writing the report, and M. C. Hill for his help in collecting data.

APPENDIX

Table 1A. Analyses of HF from the Hydrofluorinator Vapor Generator[a]

Component	Composition of HF[b] Run Number T-2	Run Number T-6
HF	98.4 wt %	98.9 wt %
H_2O	1.35 wt %	1.0 wt %
S	< 50	< 50
Zr	< 5	c
Na	< 5	10
Li	< 5	c
Cr	< 2	0.5
Mo	< 1	c
Ni	1	2
Cu	0.1	5
Sn	< 2	c
Fe	5	5
Mg	0.5	0.8
Si	2	1

[a]From ORNL-CF-60-12-19.

[b]Analyses given in ppm unless stated otherwise.

[c]Below limit of detection.

Table 2A. Analyses of Fluorine[a]

F_2	O_2 and/or N_2	HF[b]
89%	7%	4%

[a]Three-month average - private communication, W. H. Taylor, Oak Ridge Gaseous Diffusion Plant, May 28, 1964.

[b]Fluorine was passed through a NaF trap to remove HF before being used in the fluorinator.

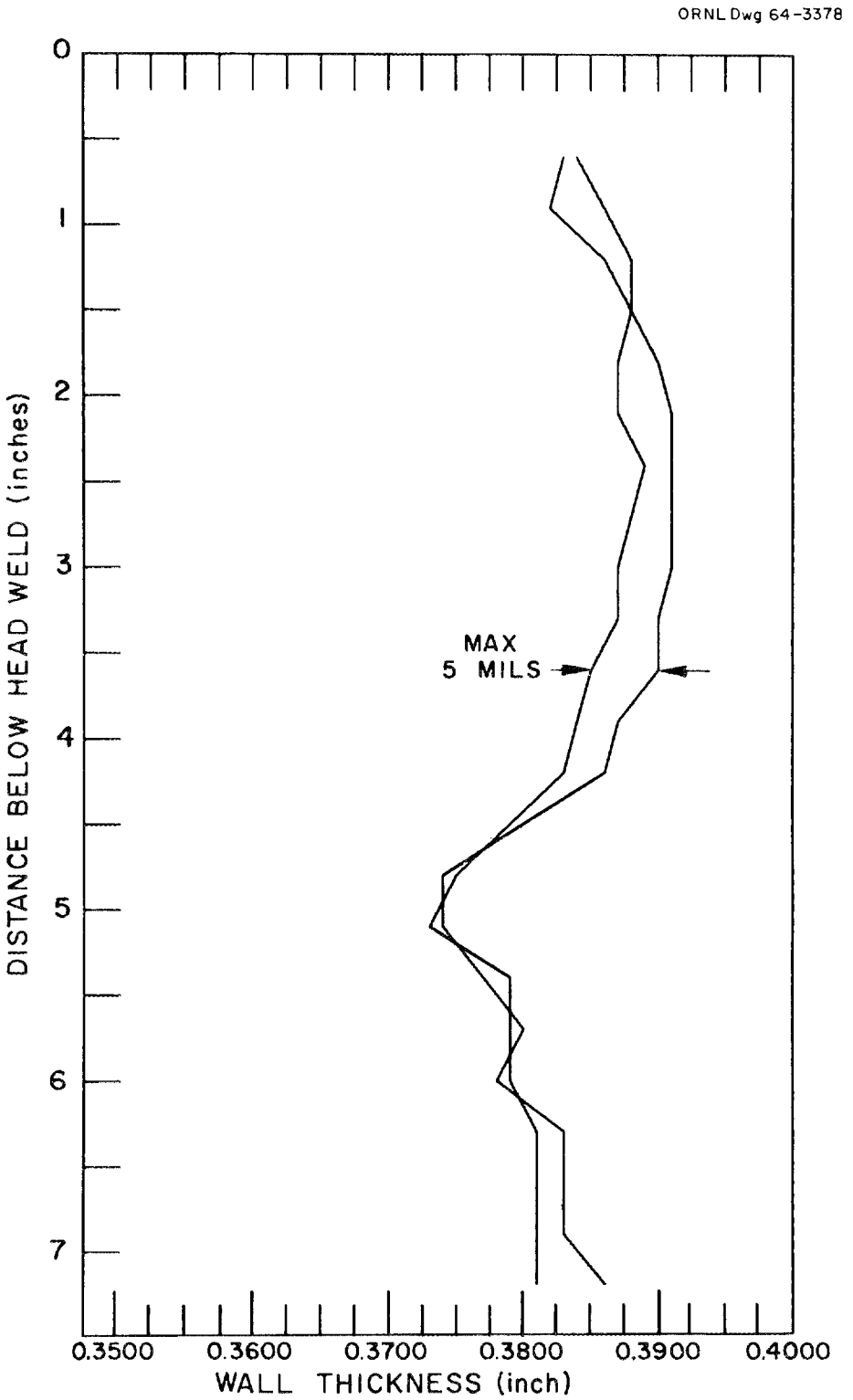

Fig. 1A. Duplicate Measurements Made in the Hydrofluorinator to Indicate the Precision of the Pulse-Echo Technique.

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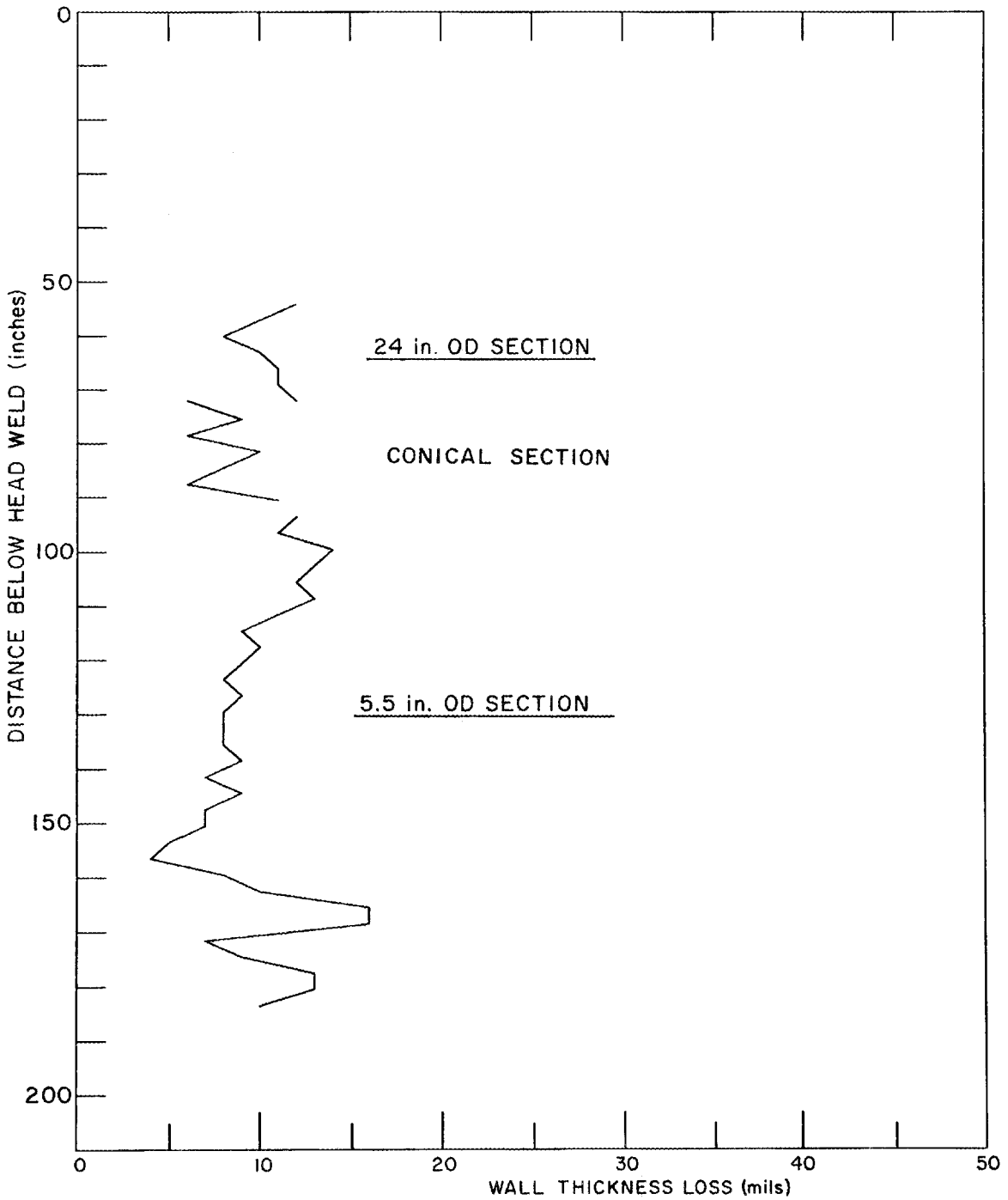

Fig. 2A. Hydrofluorinator Wall-Thickness Losses After 29 Runs.

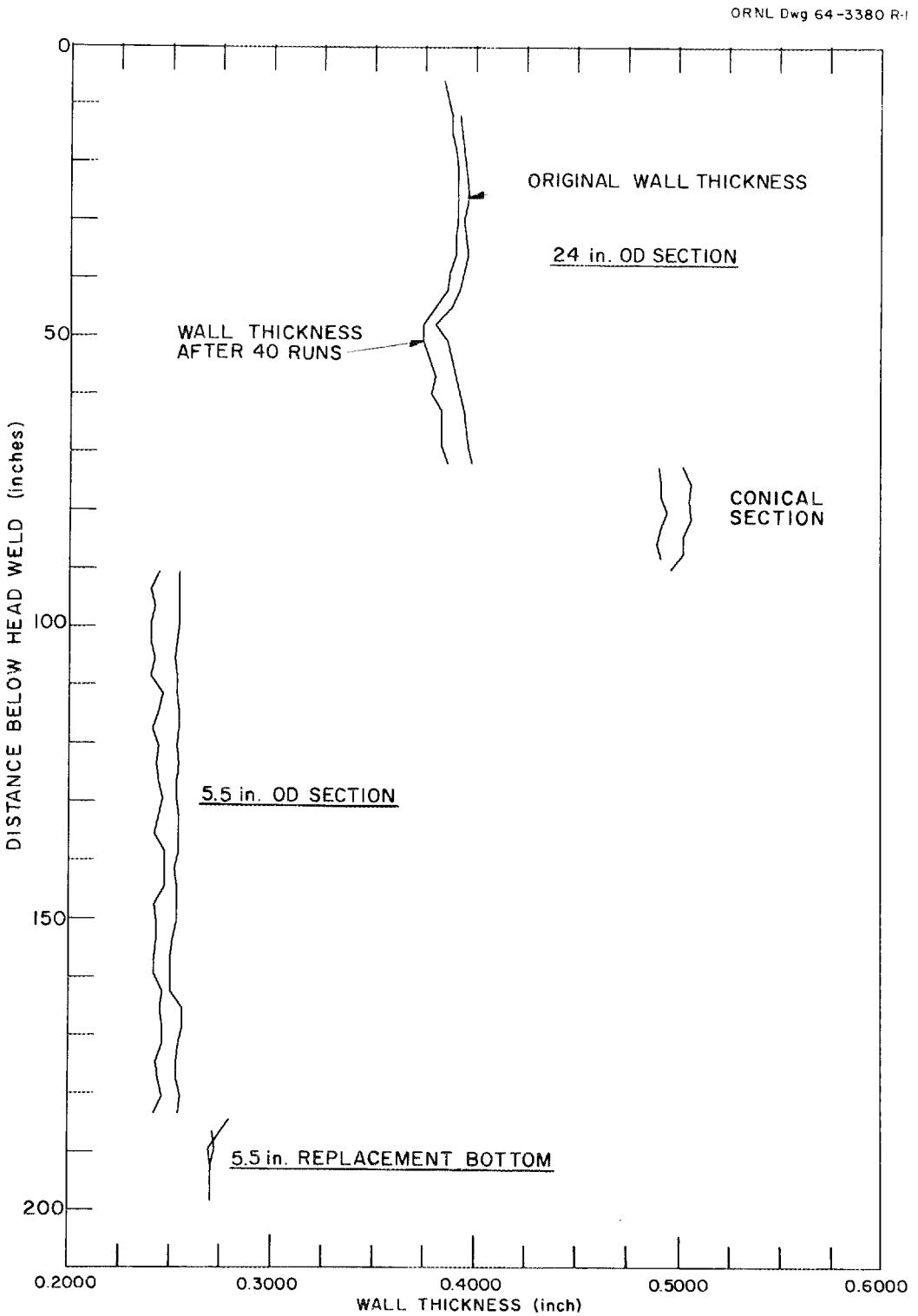

Fig. 3A. Hydrofluorinator Wall-Thicknesses Before and After 40 Zirconium Runs (North Wall).

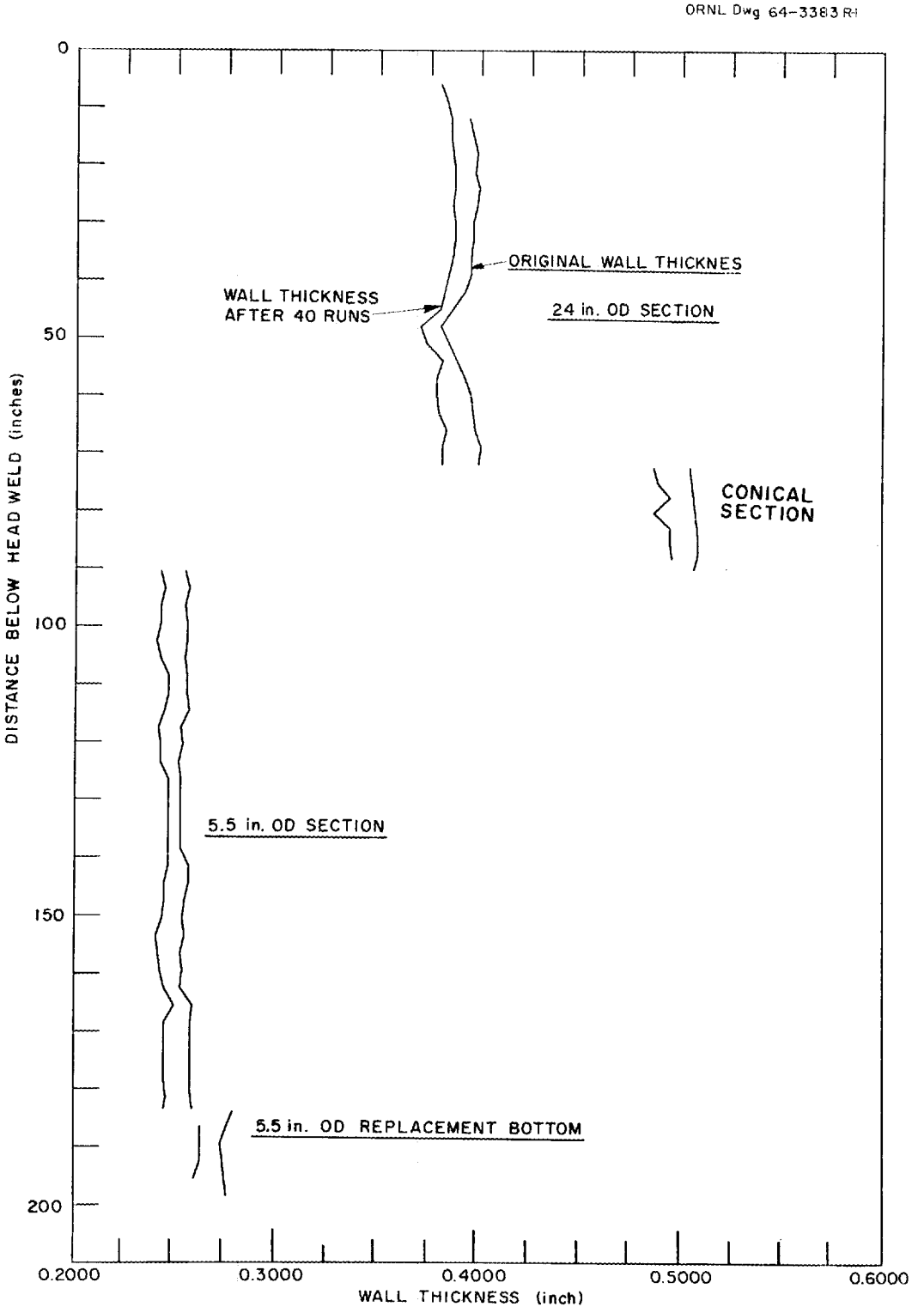

Fig. 4A. Hydrofluorinator Wall Thicknesses Before and After 40 Zirconium Runs (South Wall).

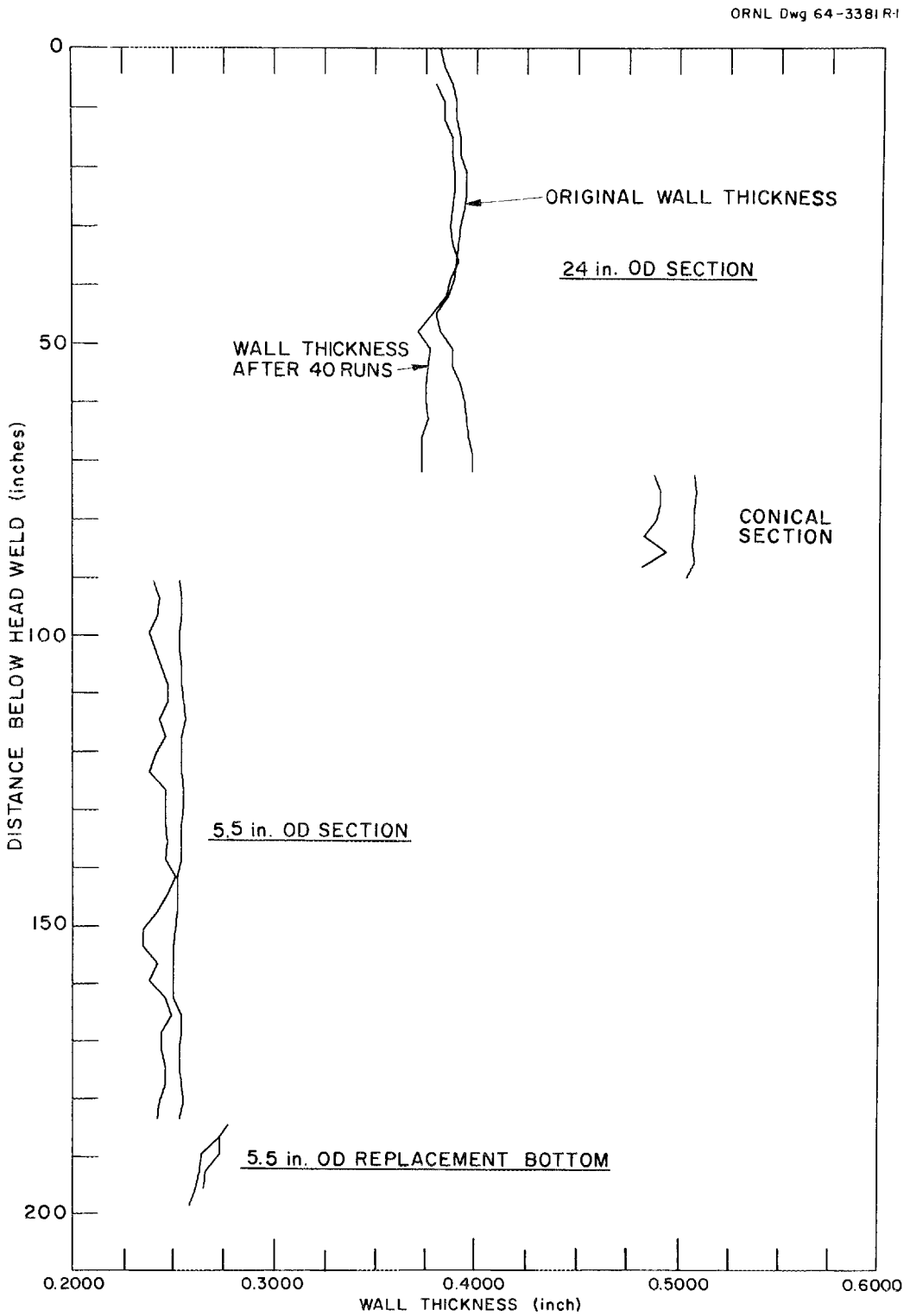

Fig. 5A. Hydrofluorinator Wall-Thicknesses Before and After 40 Zirconium Runs (East Wall).

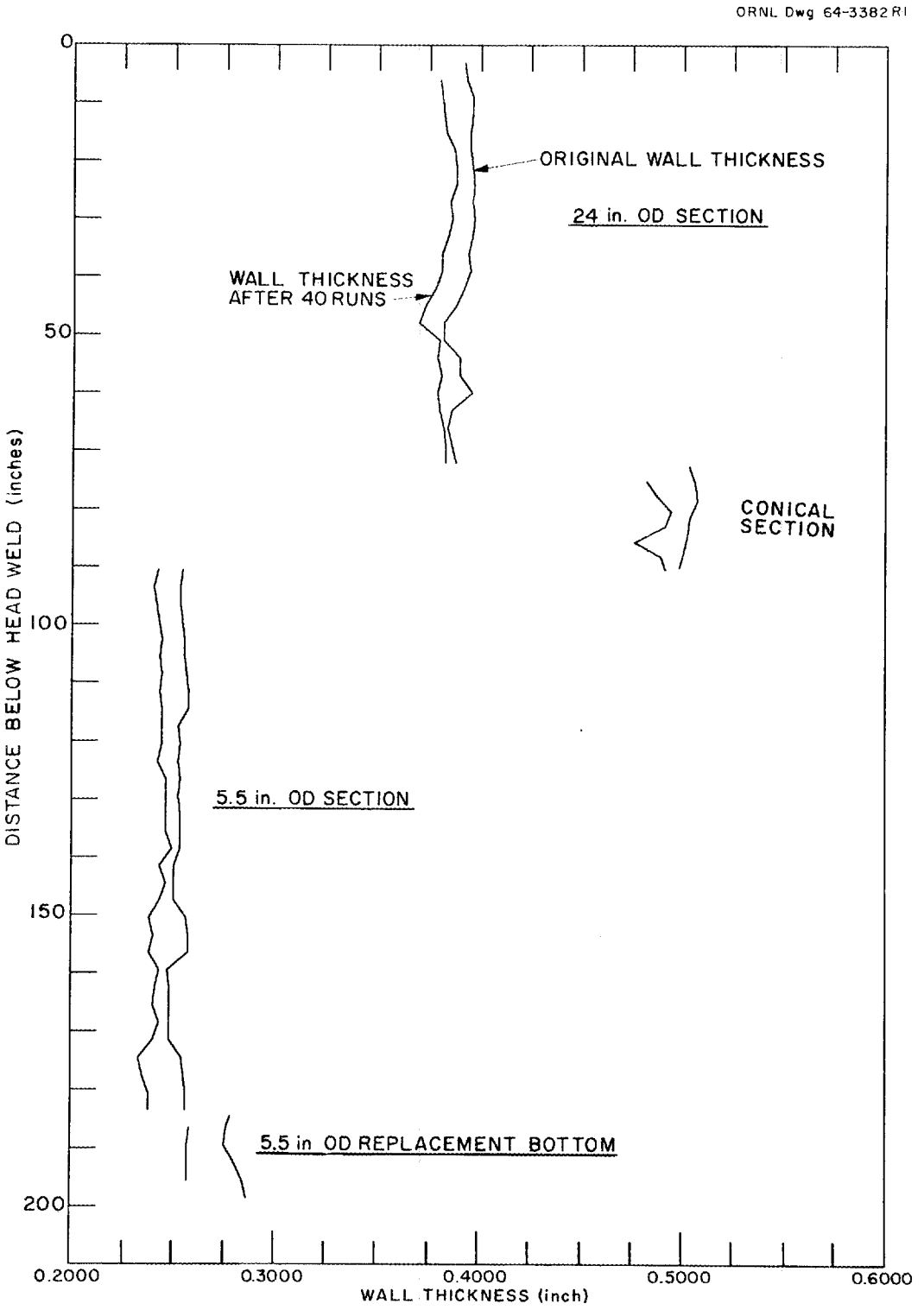

Fig. 6A. Hydrofluorinator Wall Thicknesses Before and After 40 Zirconium Runs (West Wall).

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