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CONSTRUCTION MATERIALS FOR THE HYDROFLUORINATOR OF THE FLUORIDE-VOLATILITY PROCESS

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TABLE OF CONTENTS

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Fuel elements clad with zirconium, or containing zirconium as a diluent, can be recovered by a fluoride-volatility process. The first step consists of hydrofluorination of the elements in a bath of molten fluoride salts using an HF sparge. In this case the two salt systems considered were $NaF\text{-}ZrF_4$ *and NaF-LiF. Nine materials were evaluated at Battelle for possible use in the construction of this hydrofluorinator: Inconel, "A" Nickel, copper, silver, Monel, Hastelloy B, Hastelloy W, INOR-1 and INOR-8. The metals were exposed to molten fluoride salts through which HF was bubbled continuously.*

The data indicate that the NaF-LiF systems are much more corrosive than the $NaF\text{-}ZrF_4$ *system. The systems are most corrosive when the alkali fluoride component is high. An elevation in temperature increases the corrosion significantly as does an increase in the HF flow rate. Hydrogen in the HF flow stream retards the corrosion of the sodium-zirconium salts significantly, but appears to have less effect on the sodium-lithium systems.*

The areas at the interface of the liquid and vapor phases were most seriously damaged under the exposure conditions usually used. However, appreciable reduction in attack was experienced when zirconium was actually hydrofluorinated.

INOR-8 was the most promising of the materials evaluated.

INTRODUCTION

A considerable amount of development work has been done at ORNL and ANL on a fluoride-volatility process for recovering uranium from spent fuel. In the first step in this process, the fuel elements are dissolved by hydrofluorination in a molten fluoride-salt bath using an HF sparge.

As might be expected, the selection of container materials capable of withstanding the corrosive attack of these operating conditions is an important part in the successful development of the process. An evaluation program for such materials was carried out as a program of assistance to the Chemical Technology Division of ORNL.

EXPERIMENTAL WORK

General Procedure

Candidate materials were evaluated under conditions simulating as nearly as possible those that might exist in an actual hydrofluorinator. Figure 1 is a schematic

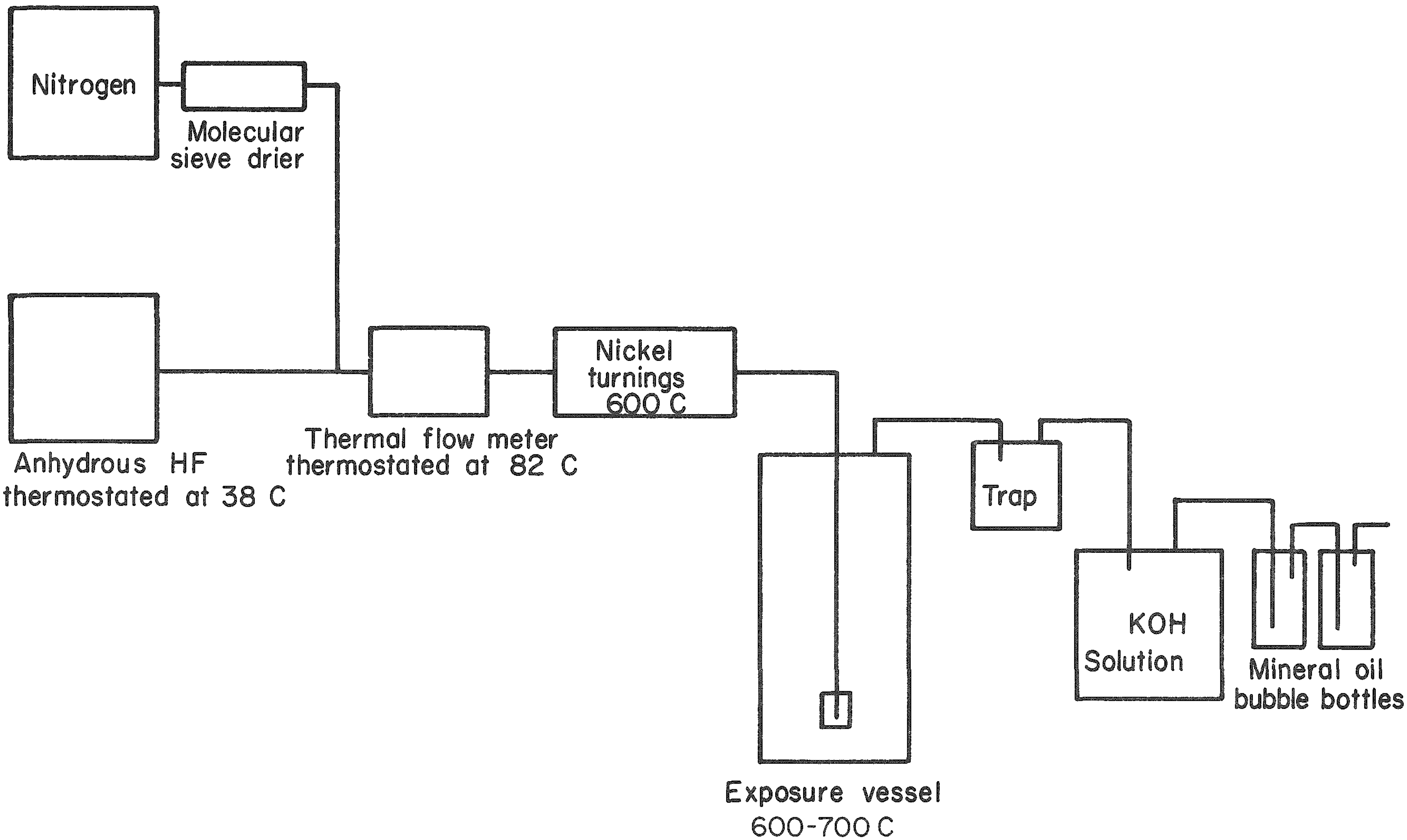


FIGURE 1. SCHEMATIC DIAGRAM OF CORROSION TEST ASSEMBLY

diagram showing the arrangement of the apparatus used. The objective was to expose metals to molten fluoride salts at elevated temperatures while sparging with purified HF. The cylinder furnishing the gaseous HF was immersed in an oven thermostatted at 38 C. The oven and tank were placed on a platform balance so that HF consumption could be followed. Special thermal flowmeters, supplied by ORNL, were used to measure the gas flow. The flow was adjusted by a Hoke No. M343 Monel valve, which has a special 1-deg taper at the closing cone. Both the valve and flowmeter were placed in a small oven maintained at 82 C.

The gas was passed through a nickel tube, about 3/4 in. in diameter and 18 in. in length, filled with nickel turnings and heated to 600 C in an attempt to scavenge sulfur compounds.

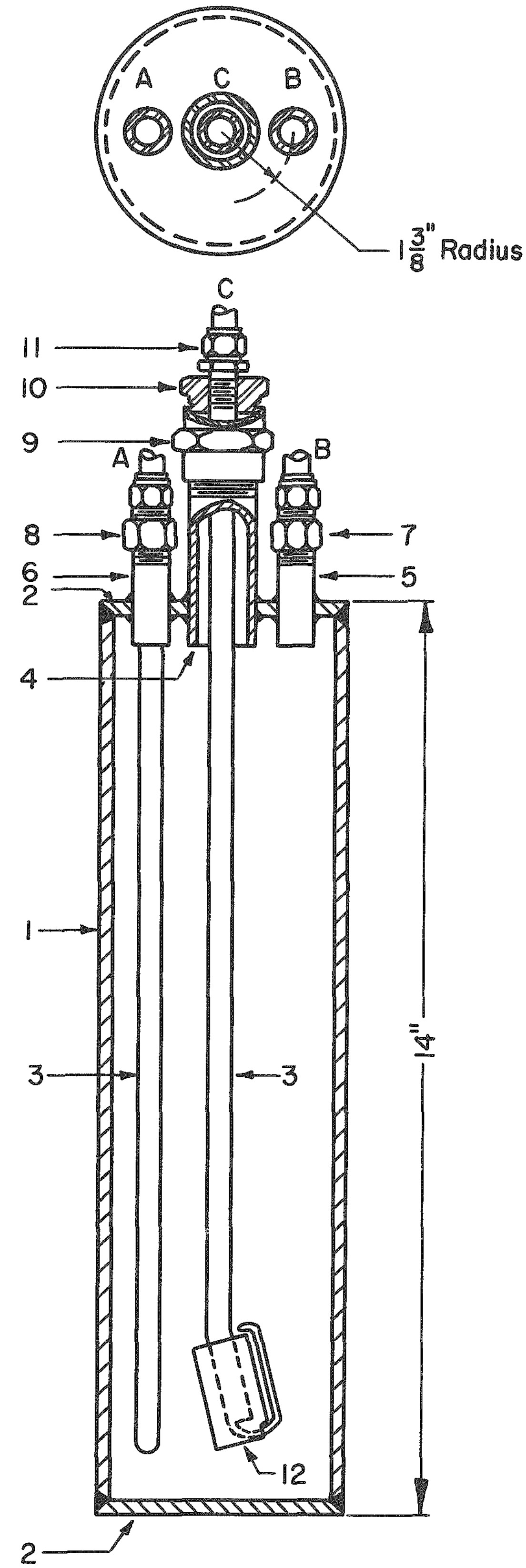
From the purification furnace, the gas was passed beneath the surface of the molten salt in the containers and allowed to bubble up past specimens inserted at various locations.

The effluent gas was passed through a copper trap and then through a battery of polyethylene bubble bottles containing mineral oil to prevent back-diffusion of air. Leaving the bubble bottles the gas was passed over the surface of an aqueous KOH solution held in a large (10 gal) polyethylene bottle, where it was largely absorbed. All inlet lines, external to the container assembly, were nickel. All valves were Monel. Effluent lines were copper or polyethylene. Thermocouples were Chromel-Alumel. Swagelok fittings permitted raising and lowering the thermocouples and sparge tube through the salt as desired. Two or three complete assemblies were usually available so that several experiments could be run simultaneously.

The first studies were made in Inconel containers furnished by ORNL. Figure 2 shows the dimensions of these containers and the method used for mounting a single specimen. In these studies the specimens were cut into 2-in. lengths from welded tubes made from the material being evaluated. They were mounted at the end of the sparge tube in such a manner that the gas bubbles would sweep over the inner surface of the tube. A slot cut in the end of the tube assured a fixed position at all times. These were called gas-impingement specimens.

Nine runs were made with these containers and it was apparent that enough "snow" (presumably ZrF_4) was carried in the effluent stream to cause plugging of the lines at varying intervals. The containers were then modified by removing their top sections and welding on each a 12-in. length of Inconel pipe of the same diameter as the bottom. The top section was flanged, baffled, and water cooled. This arrangement eliminated carry-over of snow to the effluent lines and permitted operation for 1000 hr at a time.

The preliminary studies showed that Inconel was appreciably attacked by the $NaF-ZrF_4$ system. Six new containers were then constructed from Hastelloy B, which other experience with fluoride salts indicated would be resistant to corrosion. Figure 3 is a drawing giving the dimensions of such an assembly. Figure 4 is a photograph of an empty container and closure. The exit arm was packed with clean copper wool to trap any "snow" which might pass the baffle or cold wall of the container. The cylinder connected to the exit arm was made from copper and was placed in the circuit to trap the small amount of azeotropic $HF-H_2O$ which usually formed. The nickel baffle



Nozzle schedule	
Nozzle	Service
A	Thermocouple well
B	Gas outlet
C	Gas inlet

Legend

1 - Inconel pipe, 4" NPS, schedule 40, $13\frac{1}{2}$" long.

2 - Inconel plate, $\frac{1}{2}$" x $4\frac{1}{2}$" O D, 2 required.

3 - Tube, $\frac{1}{4}$" O D x 0.035" wall thickness.

4 - Pipe, 1" NPS, schedule 40, $4\frac{1}{2}$" long.

5 - Pipe, $\frac{1}{4}$" NPS, schedule 40, $2\frac{1}{2}$" long.

6 - Pipe, $\frac{3}{8}$" NPS, schedule 40, $2\frac{1}{2}$" long.

7 - Adapter, $\frac{1}{4}$" NPS x $\frac{1}{4}$" O D tube.

8 - Adapter, $\frac{3}{8}$" NPS x $\frac{3}{8}$" O D tube.

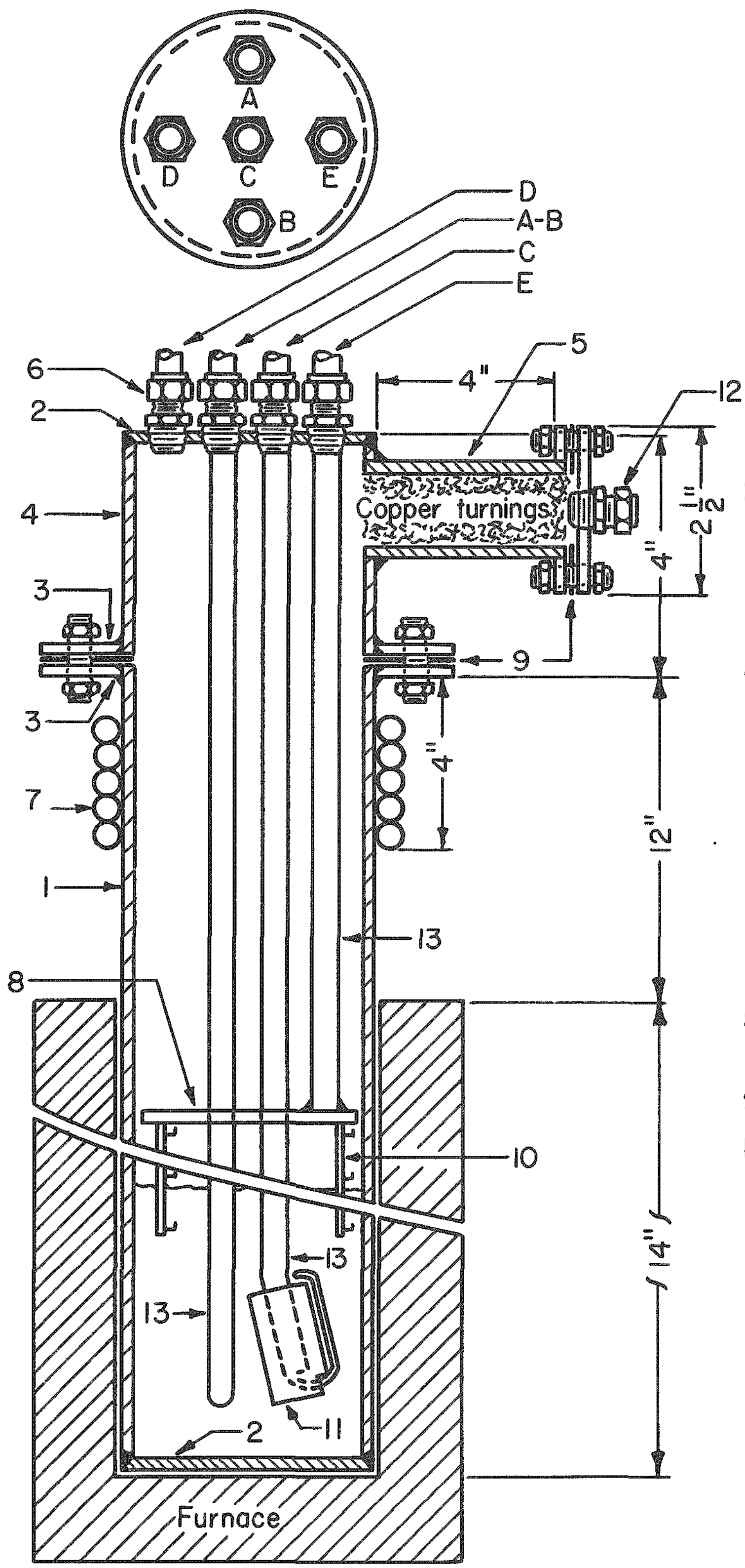
9 - Union, 1" NPS - 125 # std.

10 - Reducing bushing, 1" x $\frac{1}{4}$" NPS.

11 - Adapter, $\frac{1}{4}$" NPS male x $\frac{1}{4}$" O D tube.

12 - Impingement specimen.

FIGURE 2. INCONEL-CONTAINER DESIGN AND METHOD FOR MOUNTING THE SPECIMEN



Nozzle schedule	
Nozzle	Service
A	Thermocouple
B	Thermocouple
C	Gas inlet
D	Pressure differential transmitter, and emergency exhaust.
E	Baffle tube

Legend

1- Hastelloy B pipe, 4" NPS, schedule 10, 26" long.

2- Hastelloy B plate $\frac{3}{8}$" x $4\frac{1}{2}$" O D, 2 required.

3- Hastelloy B plate (flange) $\frac{1}{4}$" flange plates 7" O D, 2 required.

4- Hastelloy B pipe 4" NPS, schedule 10, 4" long.

5- Hastelloy B pipe 1" NPS, schedule 40, 2" long.

6- Monel adapter, $\frac{1}{4}$" NPS male x $\frac{1}{4}$" O D tube, 5 required.

7- *Copper $\frac{1}{4}$" tubing cooling* coils, brazed to tube wall.

8- Baffle plate, $3\frac{1}{2}$" diameter x 0.045" thick.

9- Polyethylene gaskets.

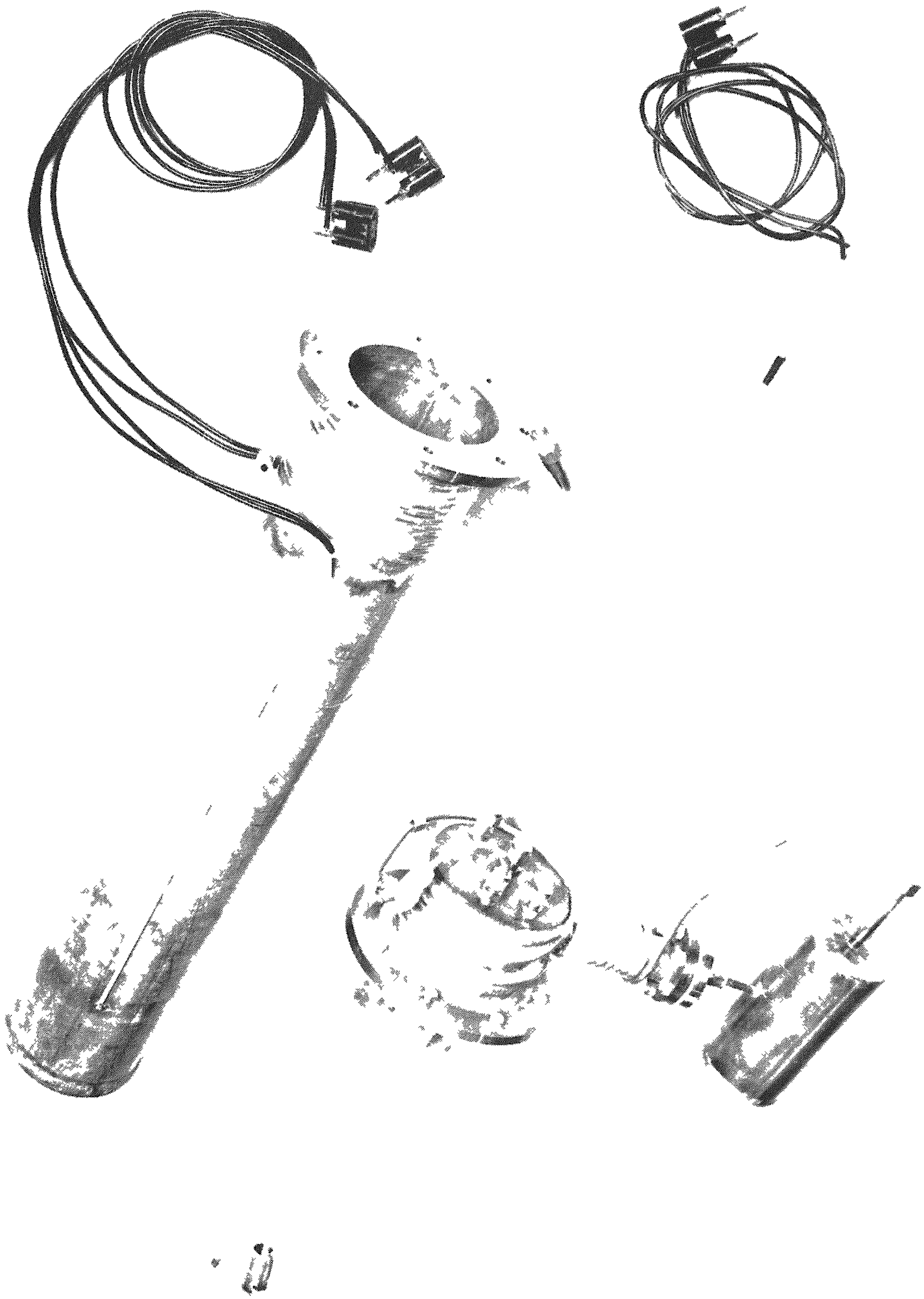
10- Coupon specimen support $\frac{1}{4}$" O D, Hastelloy B tube with Inor 8 wire hooks.

11- Impingement specimen.

12- Off-gas exhaust.

13- Hastelloy W tube, $\frac{1}{4}$" O D x 0.035" wall thickness.

FIGURE 3. DESIGN DETAILS OF HASTELLOY B CONTAINER



N48626

FIGURE 4. HASTELLOY B CONTAINER AND CLOSURE SHOWING GAS-IMPINGEMENT SPECIMEN

plate was normally used at a lower position than shown in the photograph. It was usually placed about 4 in. above the salt level.

Figure 5 shows two assemblies in operating position in the electric furnaces. Figure 6 is a photograph of the complete arrangement from HF tank to flowmeter, purification furnace, corrosion assembly, bubble bottles, and KOH absorbers.

Corrosion Results

The initial studies were made in Inconel containers loaded at ORNL to a depth of about 7 in. with an equimolar mixture of NaF and ZrF_4.

The salt was melted under an atmosphere of nitrogen and the thermocouple well and sparge tube holding the specimen were immersed. The HF flow was started and, after about 2 hr, the nitrogen flow was stopped. The procedure was reversed at the conclusion of the run.

Following exposure, the specimens were freed from adhering salt by soaking in boiling 2.5 w/o ammonium oxalate solution.

Several materials were evaluated in this series of experiments. Table 1 lists the corrosion rates for these materials calculated from weight-loss measurements and from measurements of the amount of sound metal as revealed by metallography.

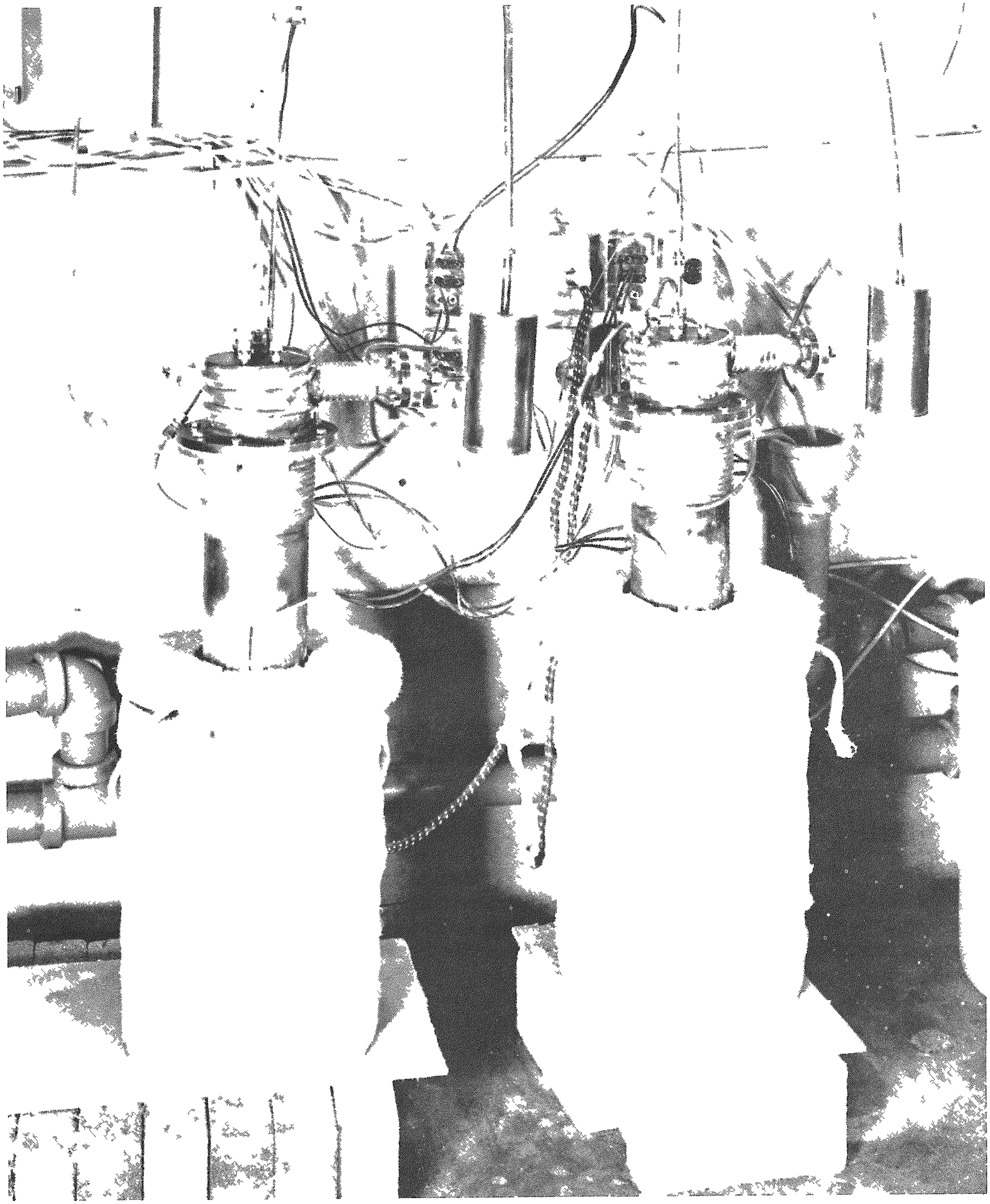
It can be seen that Inconel, "A" Nickel, and Monel showed relatively high corrosion rates. Hastelloy W, INOR-1, and INOR-8 were much more corrosion resistant.

Inconel

Metallographic sections of Inconel specimens showed that selective leaching occurred on the outer layers of the metal. The thickness of this layer was directly related to the length of time the specimen was exposed to HF in the fused salt. Figure 7 shows photomicrographs of sections from the tubes used for three of the experiments. As would be expected, the corrosion rates calculated from the sound metal shown on the metallographic specimen were much higher than those obtained from weight-loss measurements (see Table 1).

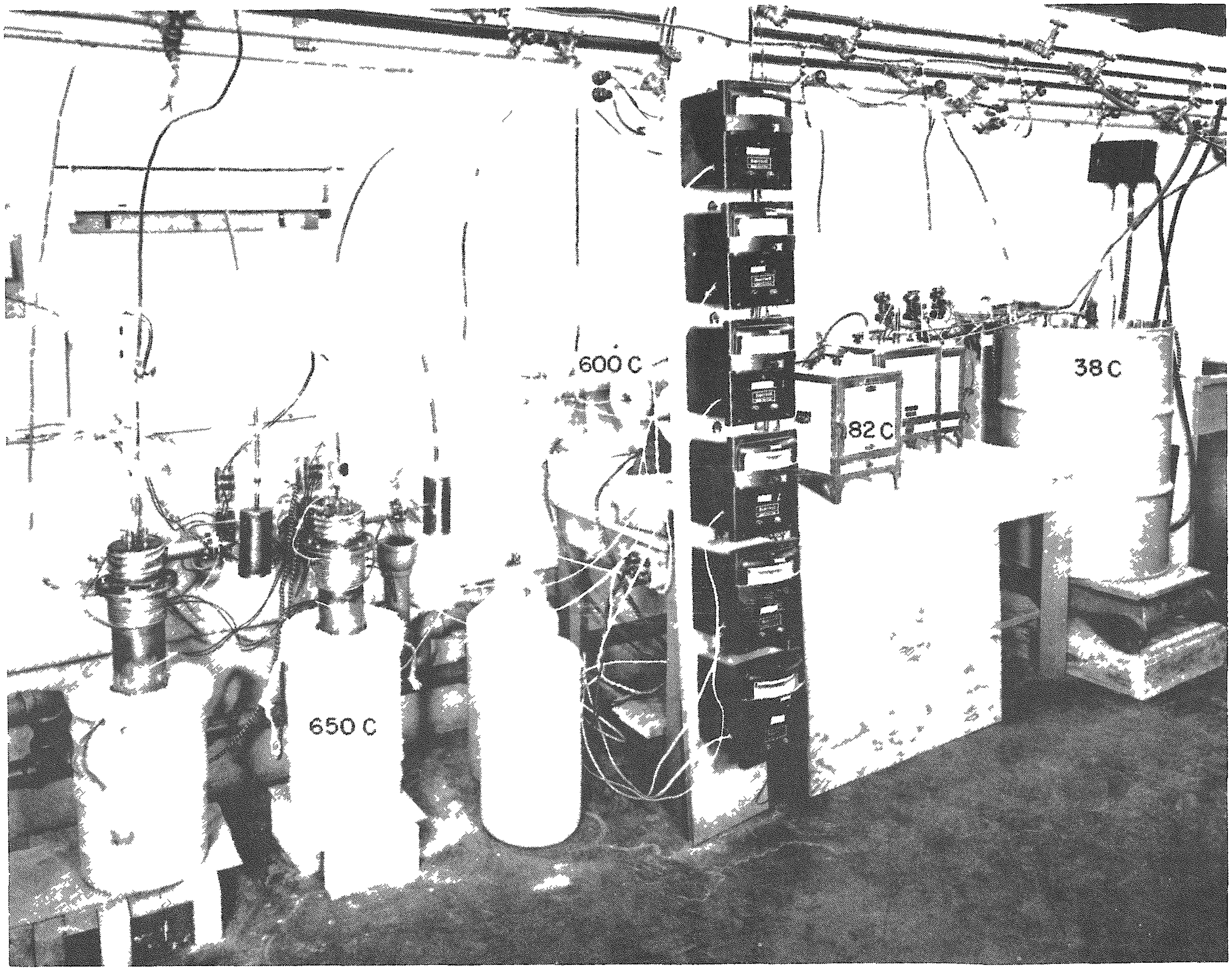
In Run 11, the Inconel tube supporting the INOR-1 specimen was severed by corrosion after about 430 hr. The specimen and Inconel tube were covered at random with clumps of metallic crystals. Figure 8 shows a portion of the sparge tube and sections of the metal crystals adhering to it. The excessive selective attack on the Inconel can also be seen. Chemical analysis showed that the metal crystals were 93.5 w/o nickel and less than 0.1 w/o chromium. The remainder was probably composed of oxides of the metals present. An analysis of a portion of the Inconel tube showed selective leaching of the chromium. The analysis showed 77.7 w/o nickel and 7.6 w/o chromium.

The salt was drained from the melt container and the container was sawed into quarters. Figure 9 shows the appearance of one of the bottom pieces. It can be seen



N48495

FIGURE 5. TWO ASSEMBLIES MOUNTED IN FURNACES



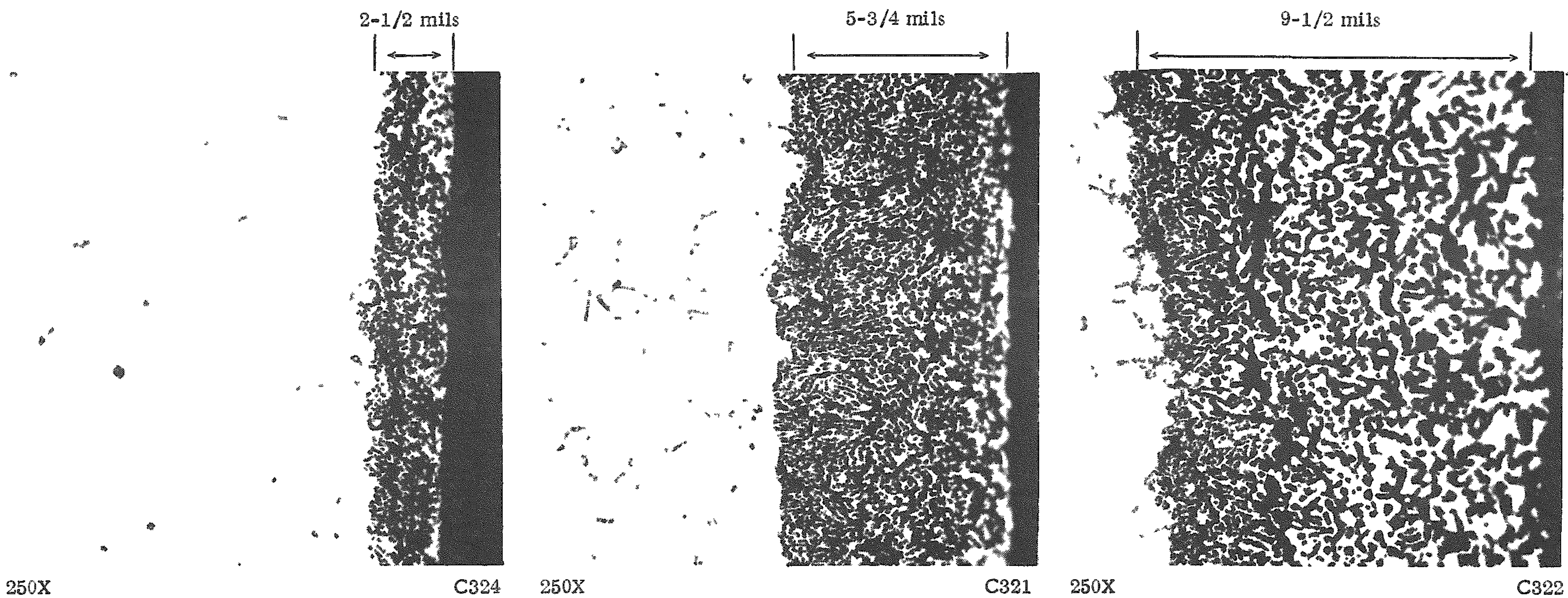
N48494

FIGURE 6. TWO COMPLETE ASSEMBLIES USED FOR HYDROFLUORINATION CORROSION STUDIES

TABLE 1. RESULTS FROM FLUORIDE-VOLATILITY RUNS CONDUCTED IN INCONEL CONTAINERS

Equimolar NaF-ZrF_4, 650 C, 10g per hr HF

Run	Container	Exposure Time, hr	Specimen Material	Corrosion Rate Determined by Method Shown, mils per month		Remarks
				Weight Loss	Metallographic Section	
1	3-1	36	Inconel	14	120	Selective leaching
2	3-1	96	Inconel	22	85	Selective leaching
3	3-1	2	Inconel	2.0	1400	Leaching proportional to exposure time
4	6-1	24	Inconel	39	--	--
5	5-1	250	Hastelloy W	Gain 80 mg	3.6	Some intergranular attack
6	2-1	250	INOR-8	0.09	1.0	Some intergranular attack
7	4-1	192	"A" Nickel	8.9	6.8	Intergranular attack
9	1-2	8	Copper	--	--	Immersion plate
10	4-1	1000	Monel	5.2	4.6-9.2	Selective attack
11	1-2	430	INOR-1	--	None	Crystal deposition
12	5-2	64	INOR-8	--	0.6	Crystal deposition
13	5-2	24	INOR-8	--	--	Few crystals
14	5-2	186	INOR-8	1.5	1.8	No crystals



Run 3, 2 Hr

Run 1, 36 Hr

Run 2, 96 Hr

FIGURE 7. PHOTOMICROGRAPHS SHOWING SECTIONS OF INCONEL SPECIMENS EXPOSED TO EQUIMOLAR $NaF-ZrF_4$ AT 650 C WITH HF SPARGE

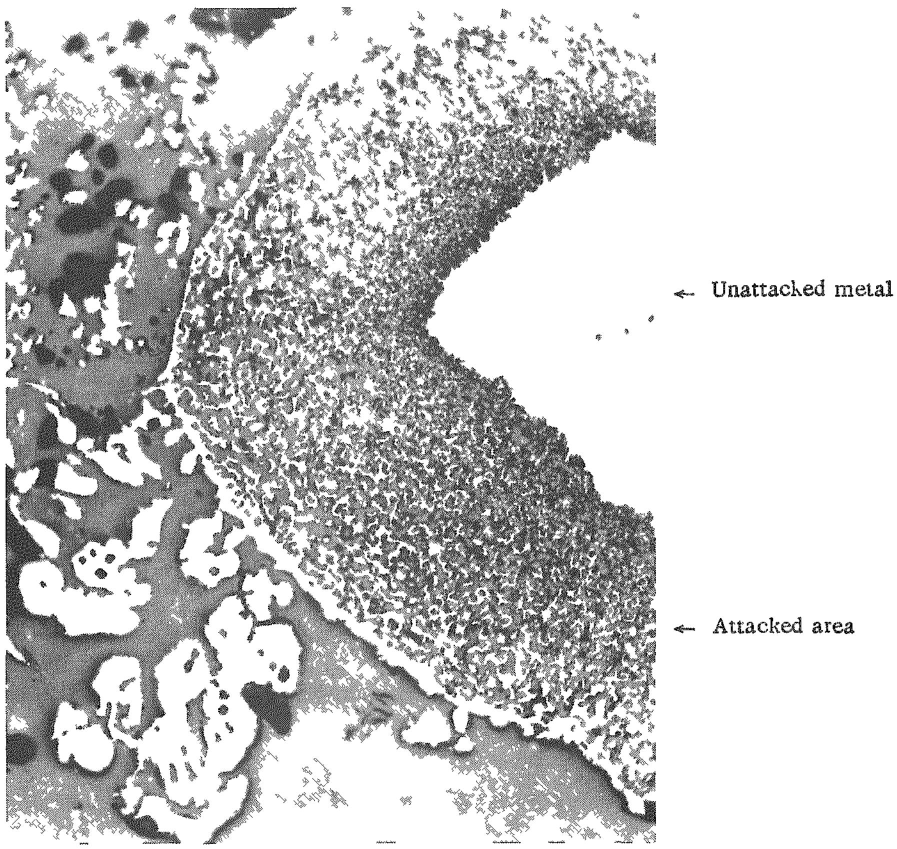
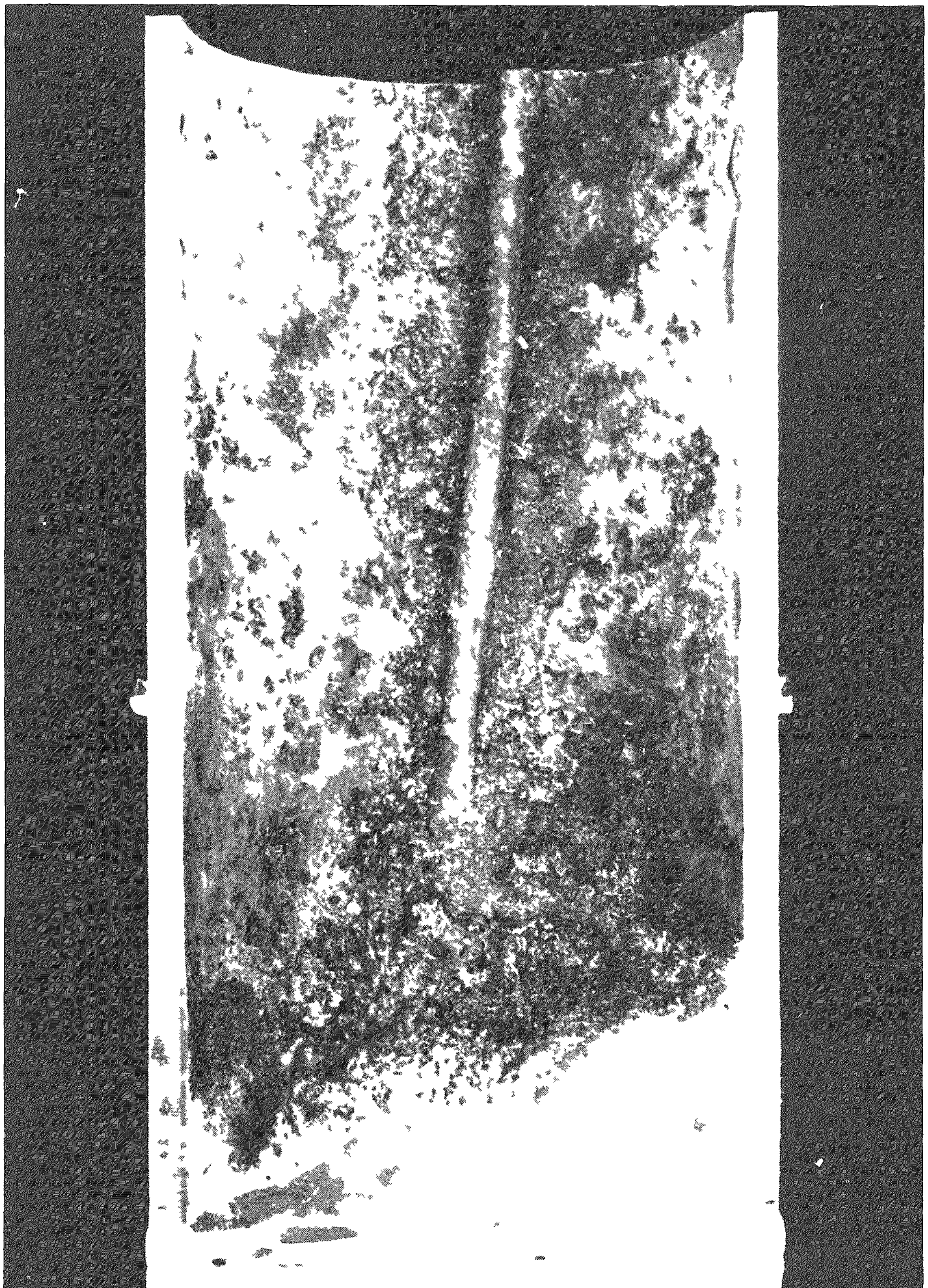


FIGURE 8. PHOTOMICROGRAPH OF SECTION OF INCONEL SPARGE TUBE WHICH FAILED IN RUN 11 AND ADHERING METAL CRYSTALS



Approx. 1X

N47008

FIGURE 9. BOTTOM SECTION OF INCONEL CONTAINER AFTER RUN 11

that a layer of metallic crystals was deposited around the inner surface. This layer reached a maximum thickness at about 7 in. from the bottom of the container and at about 4.5 in. down from the liquid line. It should be noted that the salt level was higher than normal in this container. A considerable amount of sludge, probably metal crystals, remained interspersed with salt in the bottom section of the container.

"A" Nickel

Specimens of "A" Nickel (Run 7) showed a corrosion rate of almost 10 mils per month. The attack was intergranular. Figure 10 shows photomicrographs illustrating the attack which occurred at 192 and 1000 hr.

Copper

Results for copper were inconclusive because a metallic coating was deposited on the copper specimen during the exposure. The outer portion of this layer was soluble in nitric acid and gave a confirmatory test for nickel. No confirmation for chromium was obtained on a portion soluble in hot hydrochloric acid. As shown by the photomicrograph in Figure 11a, this metallic layer was approximately 0.5 mil thick. It can be seen that grain growth occurred in the copper specimen during exposure.

Hastelloy W

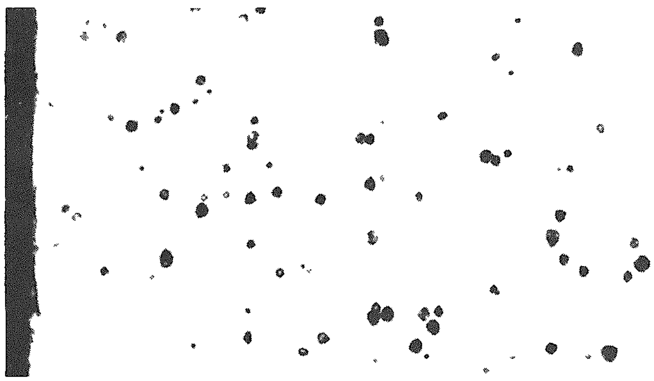
In general, Hastelloy was quite resistant to attack. Figure 11b shows that some intergranular attack was found after an exposure of 250 hr. However, subsequent work in which 1/4-in. Hastelloy W tubes were used for thermocouple wells and sparge tubes indicated that it was much more resistant than Inconel or nickel.

Monel

A Monel specimen held on a Monel sparge tube was exposed for 1000 hr. At some time during the exposure period, the sparge tube was severed by corrosion at the bent area. The penetration rate would be 25 mils per month if calculations were based on about 1000 hr. The specimen tube showed a penetration rate of 5.2 mils per month based on weight loss. Measurements made from the microsection show a penetration of 9.2 mils per month at the area swept by the gas and 4.6 mils per month at other areas. Figure 11c includes a photomicrograph of a section of the Monel sparge tube after 1000 hr of exposure. It can be seen that selective attack and roughening occurred at the surface during exposure.

Silver

Specimens of sheet silver were exposed in equipment made from Hastelloy B. Table A-2 in the Appendix shows the corrosion data obtained. Penetrations of about 7 to 9 mils per month were observed, based on weight-change values. Some difficulties were encountered because of mass transfer of silver. Crystals of the metal were deposited on other corrosion specimens and at various areas throughout the container.



250X C367

As Received

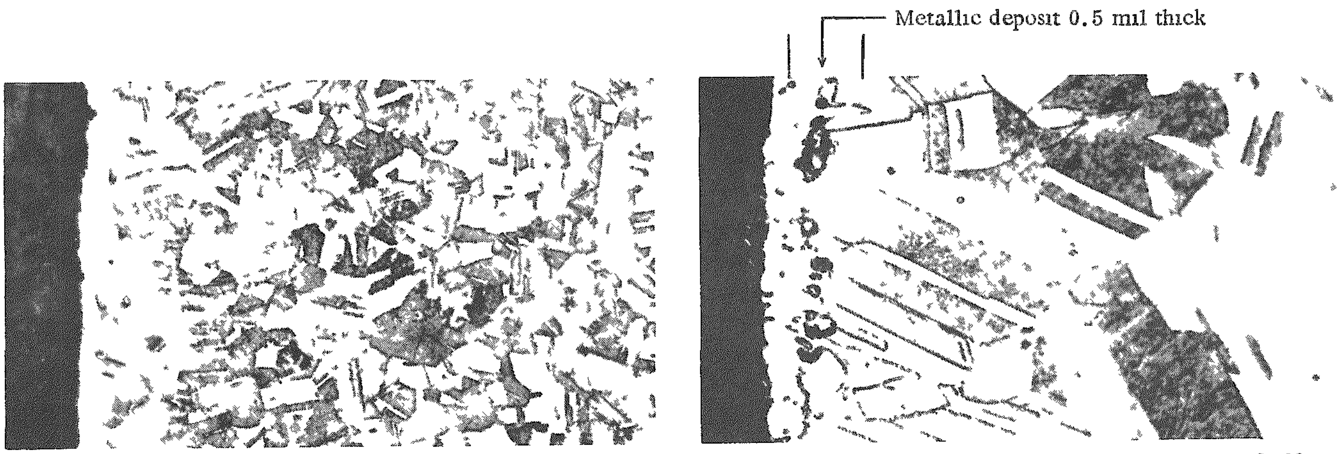
250X C366

Nickel Impingement Specimen After 192 Hr

500X C419

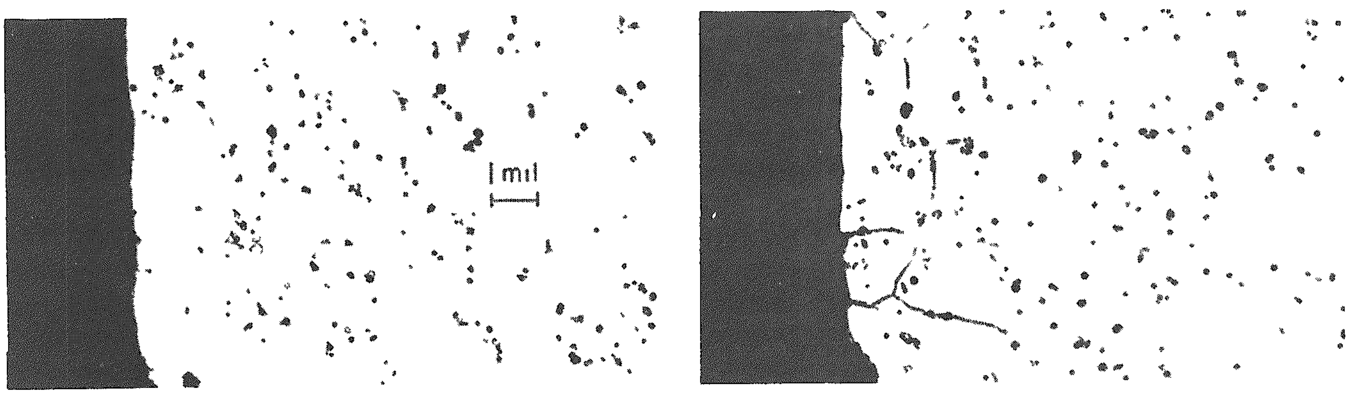
Nickel Thermocouple Tube Showing Intergranular Attack After 1000 Hr

FIGURE 10. PHOTOMICROGRAPHS SHOWING INTERGRANULAR ATTACK OF NICKEL EXPOSED TO EQUIMOLAR NaF-ZrF_4 AT 650 C



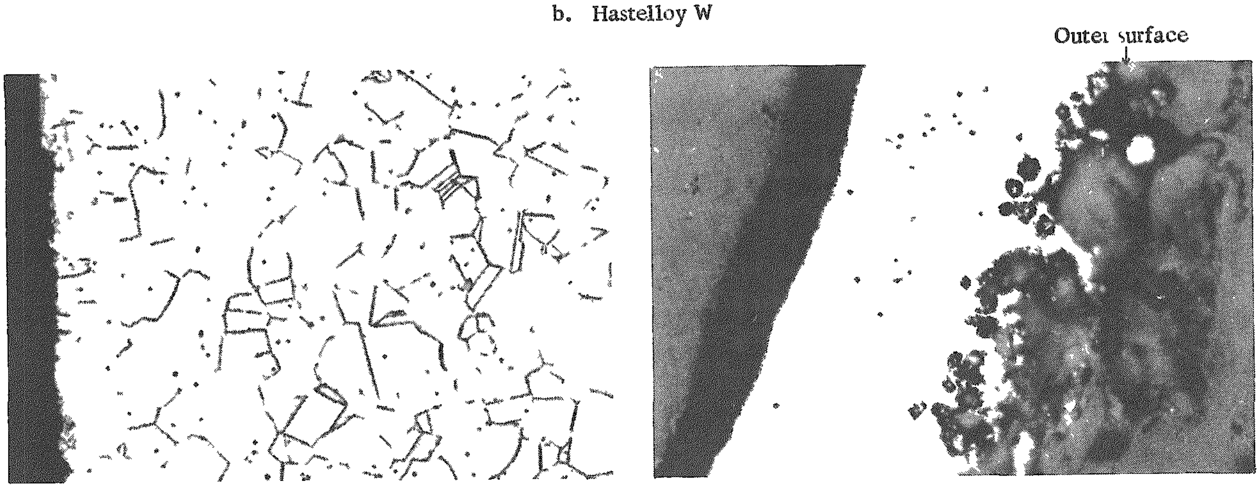
250X As Received C368 | 250X After 8 Hr C369

a. Deoxidized Copper



250X As Received C349 | 250X After 250 Hr C350

b. Hastelloy W



250X As Received C421 | 250X Sparge Tube After 1000 Hr C420

c. Monel

FIGURE 11. PHOTOMICROGRAPHS SHOWING SECTIONS OF SPECIMENS EXPOSED TO EQUIMOLAR $NaF-ZrF_4$ AT 650 C WITH HF SPARGE

Hastelloy B

Containers made from Hastelloy B have shown good service in a variety of salt compositions. Corrosion coupons of Hastelloy B were exposed during studies of INOR-8 which are described later. Table A-2 in the Appendix gives the penetration results for the Hastelloy pieces. It can be seen that its resistance is quite good in most cases. If it were not for its age-hardening characteristics and poor resistance to oxidation, it would be a top contender as a container material.

INOR Alloys

Since the initial studies showed that INOR-1 and INOR-8 were quite resistant, the work done in the improved containers made from Hastelloy B was confined largely to these materials. The containers were fitted with an easily dismountable head so that multiple corrosion specimens could readily be used. Most runs were made using tubular specimens mounted on the bottom of the sparge tube as was described earlier. In many cases, a tube of INOR-1 was also placed above the standard INOR-8 tube. In addition, coupons, approximately 1/2 by 3 in., of each of the above alloys were suspended at vapor, interface, and liquid positions. These coupons were fastened with INOR-8 wire to a 1/4-in. Hastelloy W tube extending down from the closure. On occasion, tubes of INOR-8 or INOR-1 were suspended at the interface. A coupon of Hastelloy B was included in many experiments so that an estimate of container life could be obtained.

Studies were made relating corrosion to the following variables:

(1) Salt composition

(2) Temperature

(3) Effects of atmosphere

  (a) Flow rate of HF

  (b) Addition of hydrogen

  (c) Addition of oxygen.

Table A-1 in the Appendix gives the details of the operating conditions used for these experiments.

Fluoride salts representing compositions for beginning, middle, and final stages during dissolution were studied. Two general groups were represented: the NaF-ZrF_4 and the NaF-LiF types. In the NaF-ZrF_4 type, the compositions in mole per cent were:

Beginning	62 NaF-38 ZrF_4
Middle	50 NaF-50 ZrF_4
Final	43.5 NaF-56.4 ZrF_4-0.11 UF_4.

In the NaF-LiF type the compositions studied were:

Beginning	43 NaF-57 LiF
Final	19.3 NaF-25.6 LiF-54.9 ZrF_4-0.21 UF_4

The corrosion was evaluated by weight changes, by dimensional changes, and by metallographic examinations. The results, expressed as penetration in mils per month, are summarized in Table A-1 in the Appendix. The table also includes details of the operating conditions used for each run.

It was found that invariably the corrosion was greatest at the vapor-liquid interface areas. Figure 12 shows the appearance of coupons and tubes after 263 hr under one of the more severe conditions (Run 20). The Hastelloy B melt container used in this run showed severe local attack. The bottom half of this container was sawed off and it was then split lengthwise. Figure 13 shows an enlargement of the section near the vapor-liquid interface area. Severe localized penetration is visible on the polished edges of the container wall.

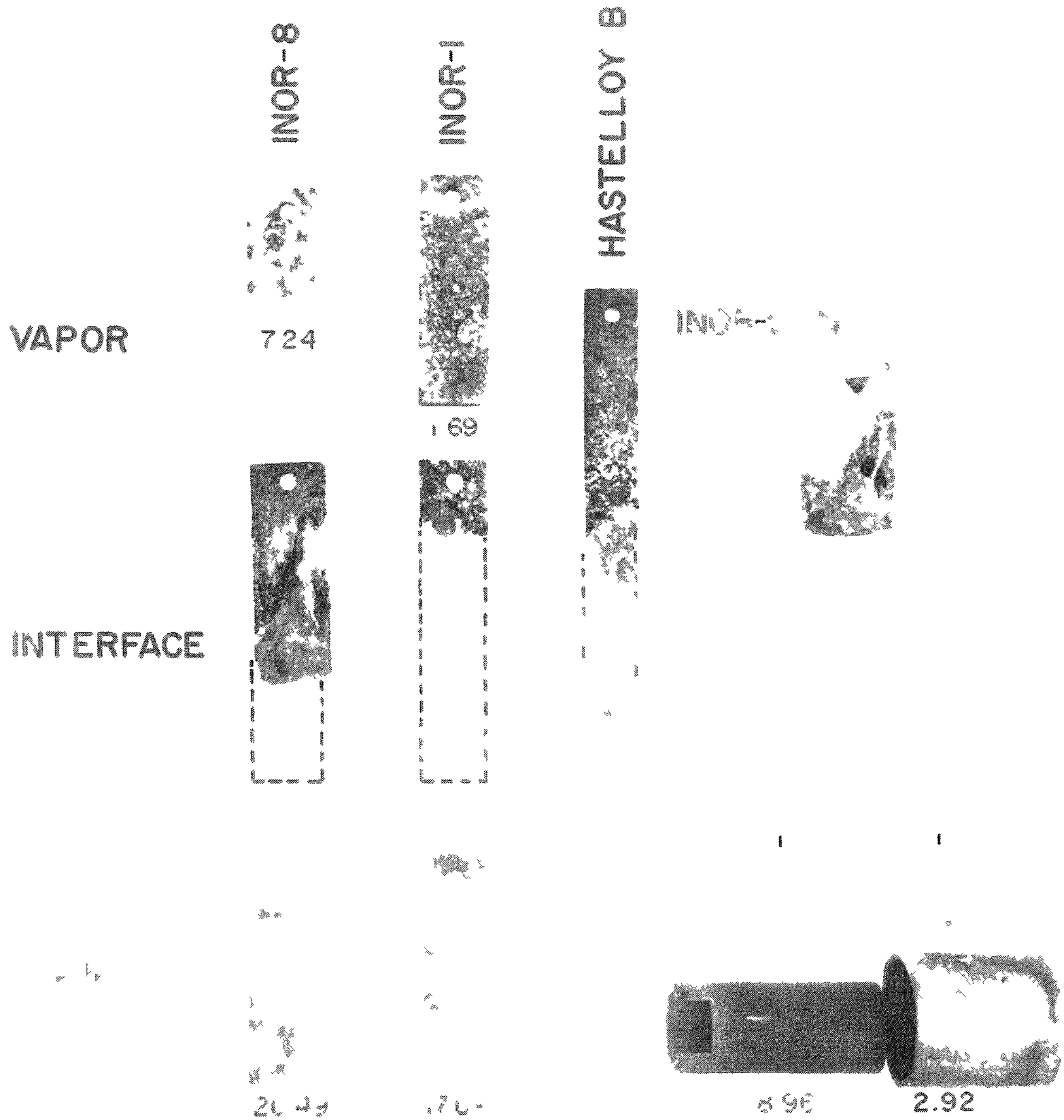
While the runs were in progress, potential measurements were made between the Hastelloy B melt containers and the insulated Hastelloy W tubes which support the specimens. The potential difference in the container with the INOR-8 specimen varied from 0.2 to 0.4 mv. These values measured with the Hastelloy B melt containers are only about 5 per cent of those previously obtained during similar measurements with an INOR-8 specimen in an Inconel container. It was under this latter condition that metallic crystals were found on the INOR-8 specimen. The implications are that the crystal deposition which occurred was not entirely a result of mass transfer but may have arisen from galvanic effects between the specimen and the container.

A 7-in. INOR-8 coupon specimen was suspended in the container during Run 24 so that it encompassed the entire range ordinarily covered by the three coupon-type specimens. Figure 14 shows a profile of the corrosion rates at various points along this specimen as calculated from thickness losses. The heavy attack on the submerged portion and the necking down at the interface are apparent. The bulge in the vapor section of the curve probably is indicative of the splash zone.

The Hastelloy W thermocouple well, sparge tube, and specimen-support tubes all showed severe attack. The thickness of the sparge tube was reduced to half of its original value at one point and the support tubes were severed at the liquid line.

Information on the corrosion behavior of INOR-8 in both sodium-zirconium and sodium-lithium systems is presented by bar graphs in Figure 15. Necking down of the specimens at the liquid line has been indicated by suitably tapering the bars. The rates indicated by solid bars are those computed from over-all weight losses. Higher rates, as determined from measurements by micrometer or by metallography, are indicated by the additional appropriate hatching of the bars.

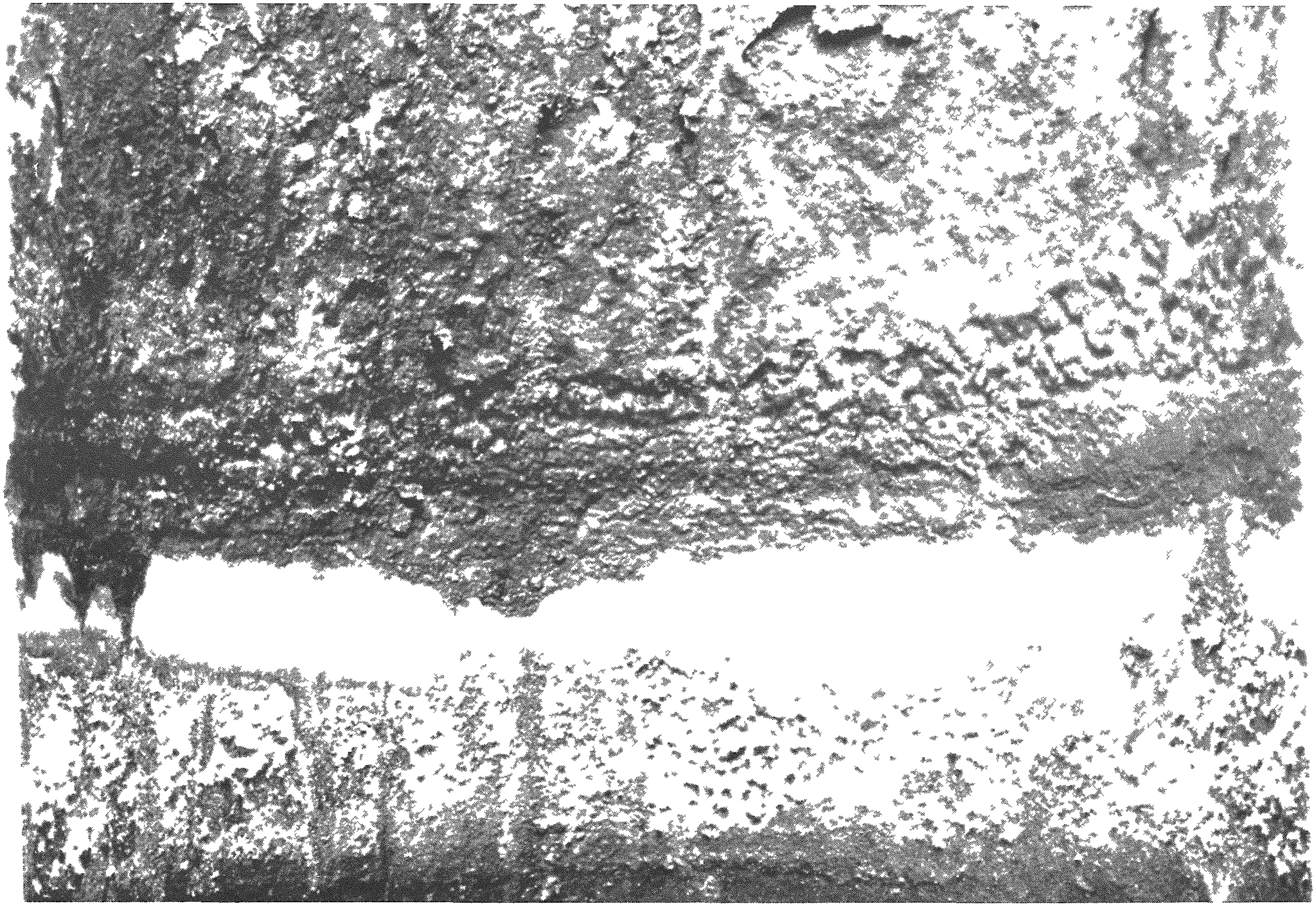
Table A-2 in the Appendix gives detailed corrosion results for all specimens evaluated in this program.



N55057

FIGURE 12. MATERIALS EXPOSED TO 43 MOLE PER CENT NaF-57 MOLE PER CENT LiF SALT AND 10 G HF PER HR FOR 263 HR AT 700 C

Corrosion rate is given in mils per month. Data were obtained in Run 20.



2X N55051

FIGURE 13. SECTION OF HASTELLOY B CONTAINER AFTER RUN 20

The area shown is at the liquid-vapor interface line. Notice the penetration into the container wall.

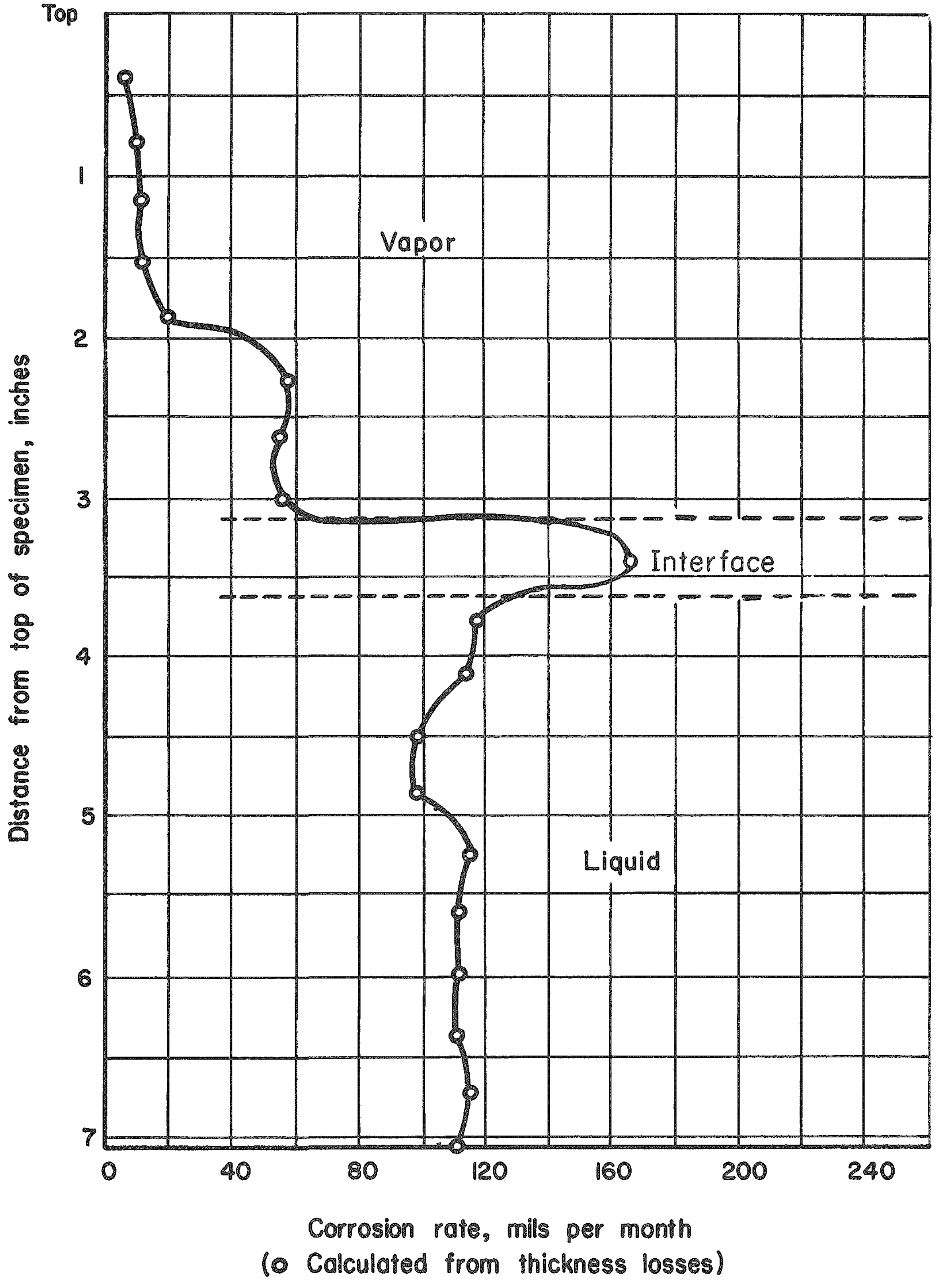


FIGURE 14. PROFILE OR CORROSION OF INOR-8 SPECIMEN EXPOSED FOR 93 HR AT 700 C TO 43 MOLE PER CENT NaF-57 MOLE PER CENT LiF SALT WITH 10 G/HR HF

Values computed from micrometer measurements of loss in thickness. Data are from Run 24.

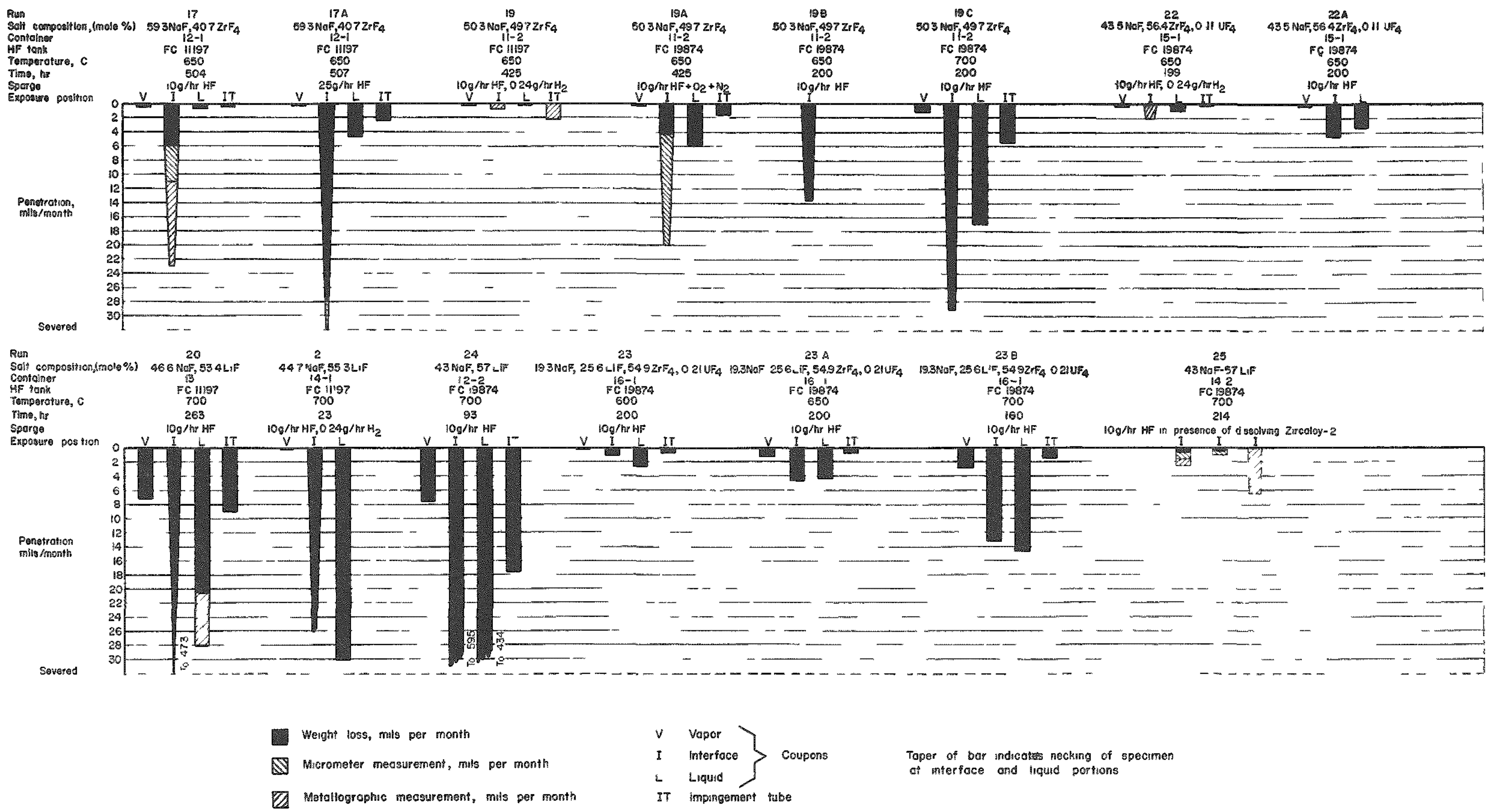


FIGURE 15. SUMMARY OF CORROSION RESULTS FOR INOR-8 IN FLUORIDE-VOLATILITY PROCESS SYSTEMS

The corrosive attack on INOR-8 material was sometimes general in nature and sometimes intergranular. Figure 16 shows photomicrographs illustrating the progressive roughening and surface attack on specimens exposed in the liquid phase caused by increased salt temperatures.

Typical intergranular attack for INOR-8 and INOR-1 material is shown in Figure 17 for interface specimens. It can be seen that the penetration is somewhat greater for the INOR-8 material in this particular experiment.

The data indicate that the sodium-lithium systems are much more corrosive to the alloys under study than the sodium-zirconium systems. An elevation in temperature increases the corrosion significantly, as does an increase in the HF flow rate. The presence of hydrogen will mitigate the corrosiveness of the sodium-zirconium salts but its effect on the sodium-lithium systems has not been fully determined.

The corrosiveness of a given salt seems to be directly related to its alkali fluoride content. In the case of the sodium-zirconium salts, three mixtures which might represent beginning, middle, and final stages of the hydrofluorination have been studied. Generally, corrosion decreases with increasing zirconium content. Possibly formation of complexes accounts, in part, for this. The exact composition of complexes at various stages in the fluoride system is not known, nor is their degree of dissociation established, but, for argument's sake, consider the complex $NaZrF_5$ known to exist to some extent. For example, in the 60 mole per cent NaF-40 mole per cent ZrF_4 salt there would be a deficit of zirconium for forming the $NaZrF_5$ complex equal to 1 mole of NaF per 2 moles of $NaZrF_5$. At the other end of the scale, i.e., 43 mole per cent NaF-57 mole per cent ZrF_4, all of the NaF could be complexed, leaving an excess of 1 mole of ZrF_4 per 3 moles of $NaZrF_5$. Of course in the equimolar salt, complete complexing with no dissociation would result in no excess of either component. The 60 mole per cent NaF-40 mole per cent ZrF_4 salt was used for Run 17, the equimolar for Run 19B, and the 43 mole per cent NaF-57 mole per cent ZrF_4 for Run 22A. Comparing the corrosion rates for these runs indicates that the hypothesis above may have some merit.

The severe localized attack which occurs at the liquid line has been noted on several occasions. In contrast to this, the impingement specimens on the sparge tube which certainly have an interface, albeit a constantly moving one, do not always show significant localized attack. Many times, coupons and their support tubes were severed at the liquid line, while little attack occurred on the sparge tube which is more directly in line with the rising HF bubbles. A possible explanation for these observations lies in gradients of temperature and composition at the liquid-vapor interface. It is known that ZrF_4 continually volatilizes from the sodium-zirconium melts. This would leave the immediate surface with a preponderance of alkali fluoride. Near the sparge tube, the agitation by the bubbling HF tends to decrease this composition gradient and, consequently, corrosion is not so severe. At the interfaces created on the impingement specimens, the opportunity for rapid replenishment of the volatilized ZrF_4 exists; consequently, the same conditions do not occur here as at the liquid line. The actual localized attack at the liquid line is undoubtedly electrochemical, arising from differences in potential between the portion of the specimen submerged and the portion at the liquid line. These differences could easily be influenced by virtue of the difference in the relative solubility of HF in the liquid phase and in the

250X C592

a. After 200 Hr at 600 C (Run 23)

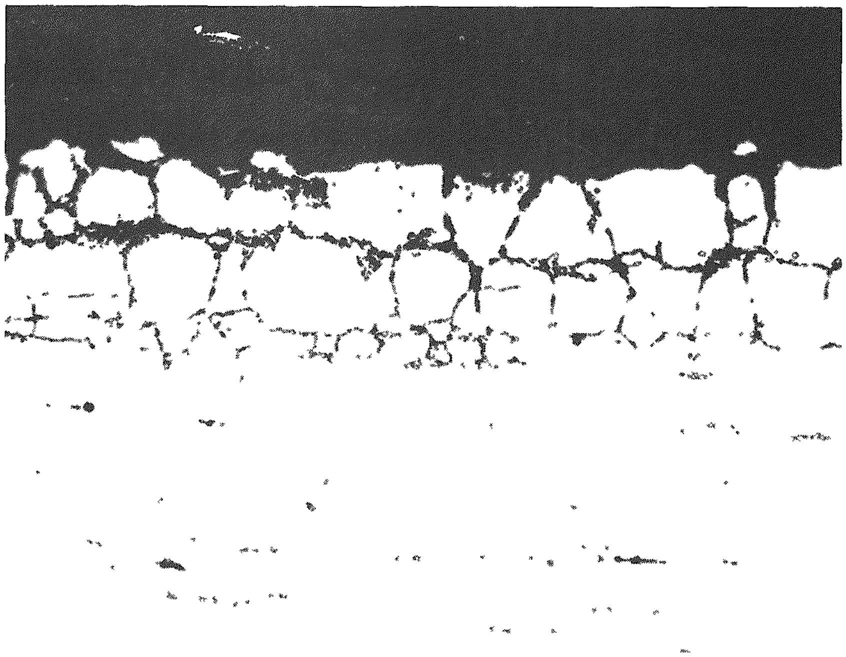
250X C593

b. After 200 Hr at 650 C (Run 23A)

250X C594

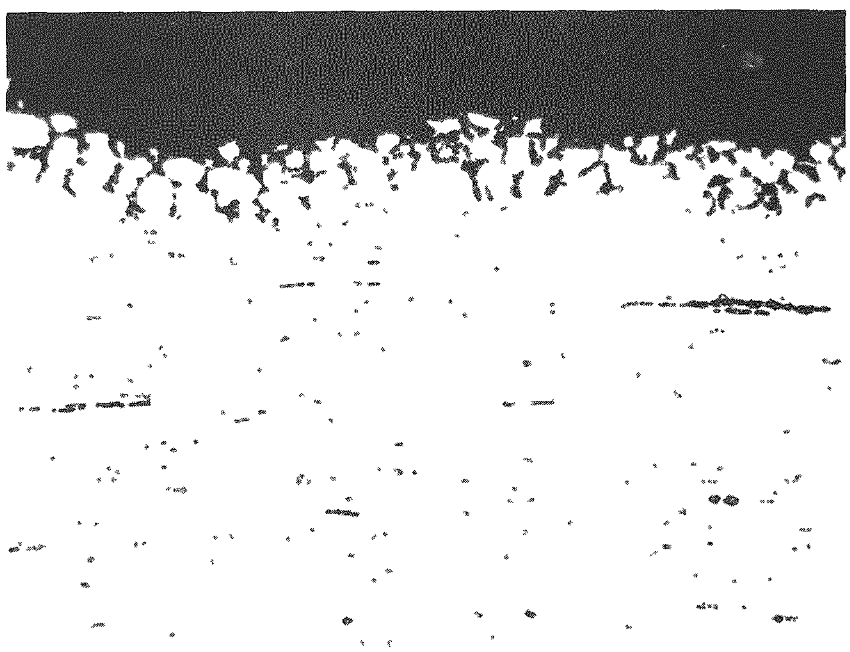
c. After 160 Hr at 700 C (Run 23B)

FIGURE 16. PHOTOMICROGRAPHS SHOWING THE ATTACK ON INOR-8 AT VARIOUS TEMPERATURES IN NaF-LiF SALTS



250X C605

INOR-8



250X C604

INOR-1

FIGURE 17. PHOTOMICROGRAPHS SHOWING INTERGRANULAR ATTACK ON SPECIMENS EXPOSED AT THE INTERFACE POSITION TO 43 MOLE PER CENT NaF-57 MOLE PER CENT LiF SALT AT 700 C FOR 93 HR (RUN 24)

partial pressure of HF in the vapor. The fact that increasing the flow of HF causes increased corrosion seems to support this mechanism. However, if one considers the lower rates on the impingement specimens with increasing flow of HF, the argument for concentration gradients at the liquid-vapor interface as a cause of the attack seems to be more reasonable.

In order to obtain a better understanding of the corrosion mechanism, an experiment was made in which dissolving Zircaloy-2 was present at all times. The objective of the work was to determine whether cathodic protection is furnished to the container (Hastelloy B) and the INOR-8 coupons by dissolving Zircaloy-2. In addition, such effects as a constant evolution of hydrogen, consumption of a portion of the entering HF stream, a gradual increase in the zirconium content of the salt, and a moving liquid-vapor interface could be examined. Work by G. I. Cathers and associates at ORNL had indicated that less severe corrosion could be anticipated under these conditions.

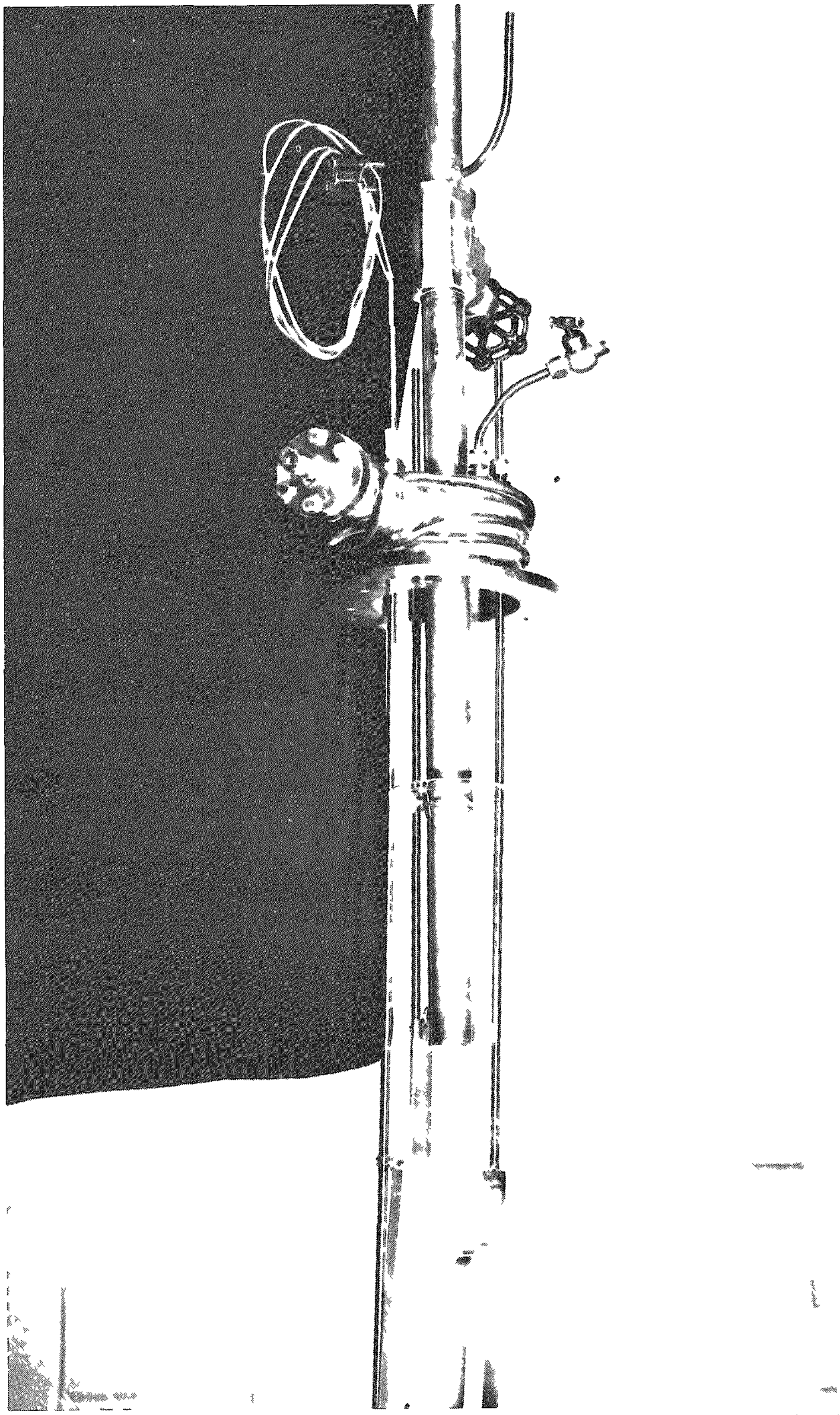
Figure 18 shows the container head and specimen-mounting arrangement used. The central pipe of 1-in. nickel was used for charging Zircaloy-2 slugs to the molten salt. A vapor-lock section located above the gate valve shown in the photograph permitted loading charges of Zircaloy-2 as desired. The vapor lock was flushed with argon continuously. Seven slugs, 0.6 in. in diameter and 1.8 in. long, weighing approximately 52 g each, were dropped simultaneously into the salt at 30 to 40-hr intervals.

Several specimens of INOR-8 were evaluated. One coupon about 5/8 in. wide and 7 in. long was attached to the thermocouple well (INOR-8, 1/4-in. tubing) with an INOR-8 wire. The photograph shows that this well was insulated from the container head by a Teflon sleeve. The thermocouple well and coupon were raised twice a day as the salt level in the container rose. Thus, the interface position was maintained at approximately the same area on the specimen. Another coupon about 11 in. long was wired to the 1/4-in. INOR-8 sparge tube and was left permanently in position during test. A double specimen was welded to the end of a third 1/4-in. INOR-8 tube. This tube was raised periodically to maintain a fairly constant interface position on the specimens. Only the thermocouple well and its attached specimen were electrically insulated from the container.

A 3 by 3-in. lap-welded coupon of INOR-8 containing a crevice was placed on the bottom of the container to obtain additional corrosion results.

The rate of dissolution was followed by three measurements. The volume of hydrogen was measured continuously with a wet-test meter after the HF had been removed. The rise in liquid level in the container was followed by dip-stick-contact measurements using the movable thermocouple well. A differential-pressure gage connected across the gas-inlet and -exit sides of the container also indicated the rise in liquid level. Figure 19 illustrates the type of data accumulated from these three measurements. The curve for theoretical hydrogen evolution was calculated on the basis of 100 per cent efficiency of dissolution at a flow rate of 9.5 g HF per hr. It may be seen that the amount of hydrogen evolved varied directly with the HF flow. The actual volume of hydrogen measured was 75 per cent of the theoretical, based on the total HF introduced.

Nine per cent of the 1980 g of Zircaloy-2 added to the salt remained undissolved on the bottom of the container at the end of the run. The final salt level was about 4 in. higher than the initial level.



N57135

FIGURE 18. SPECIMENS AND CHARGE TUBE FOR CORROSION STUDIES IN THE PRESENCE OF DISSOLVING ZIRCALOY-2

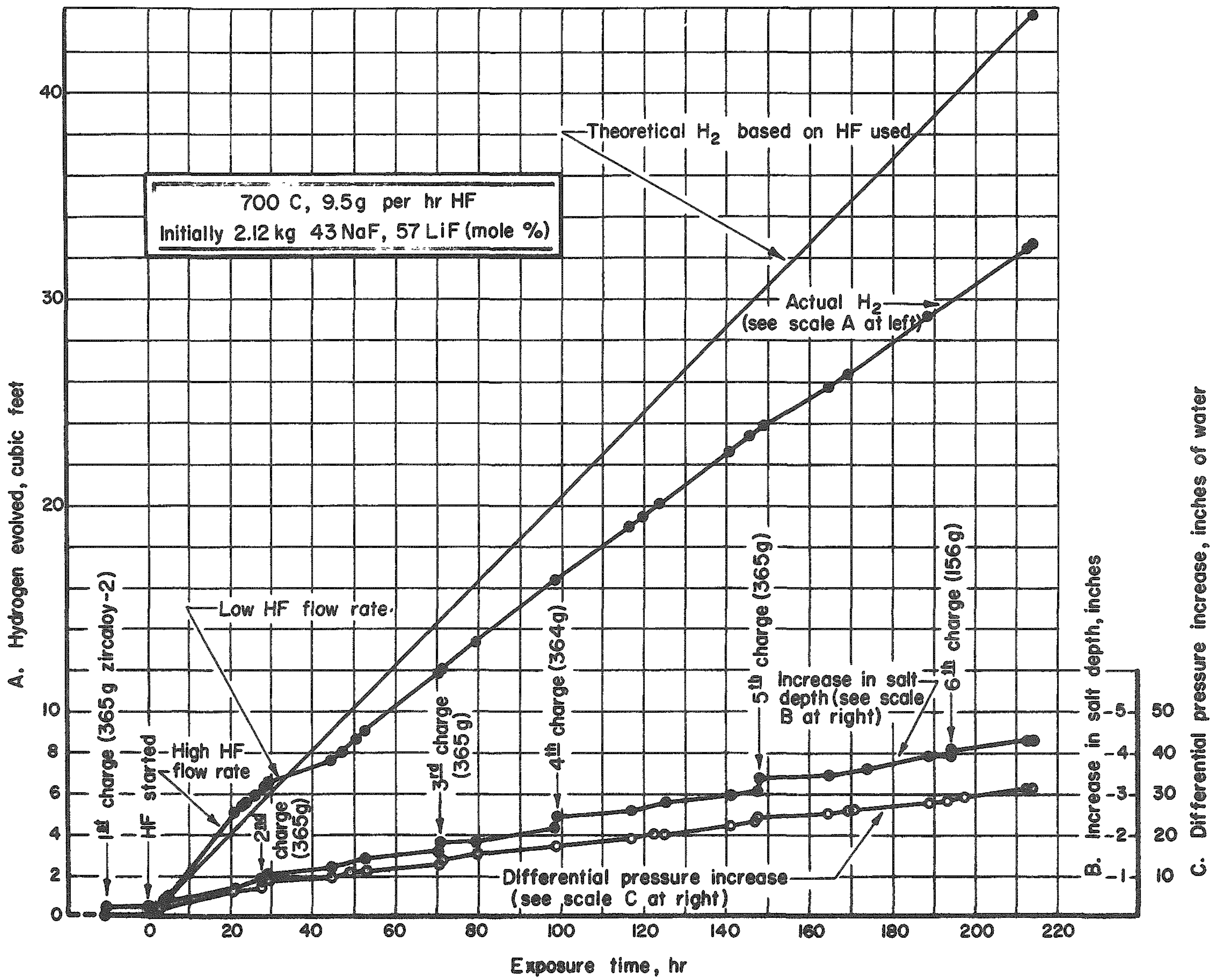


FIGURE 19. OPERATING DATA OBTAINED DURING RUN 25 WITH DISSOLVING ZIRCALOY-2 PRESENT

The over-all penetration rates obtained in this experiment were significantly lower than those from comparable runs made in the absence of dissolving Zircaloy-2. For example, in the absence of zirconium, the specimens were often severed at the interface area. In the presence of zirconium, very little interface attack was noted except at one area on the thermocouple well where about 9 mils of metal was removed (31 mils per month). Also, some thinning (7 to 23 mils per month) was noted at the interface on the straight coupon of the pair shown at the right in Figure 18.

Table 2 summarizes the penetration data obtained for eight different coupons or tubes. Weight-change data were taken on two coupon specimens. One specimen was raised periodically so that essentially a constant interface area was maintained as the liquid level rose. The corrosion rate was 0.7 mil per month. The other specimen, fastened to the sparge tube, was not moved and the corrosion rate was 0.2 mil per month.

The table also includes penetration values based on micrometer readings and on metallographic sections. The values reported are for areas where the major amount of attack was noted.

Figure 20a shows the microstructure of the INOR-8 thermocouple well at the interface area where maximum attack occurred. It can be seen that considerable roughening of the metal took place and that the wall thickness was decreased. A very slight amount of intergranular attack was noted. Figure 20b shows the lesser amount of roughening which occurred on the metal immersed in the liquid.

Figure 21a shows a section cut from the interface area of the movable, insulated coupon. A similar section from the movable, connected noninsulated coupon showed somewhat more roughening (see Figure 21b).

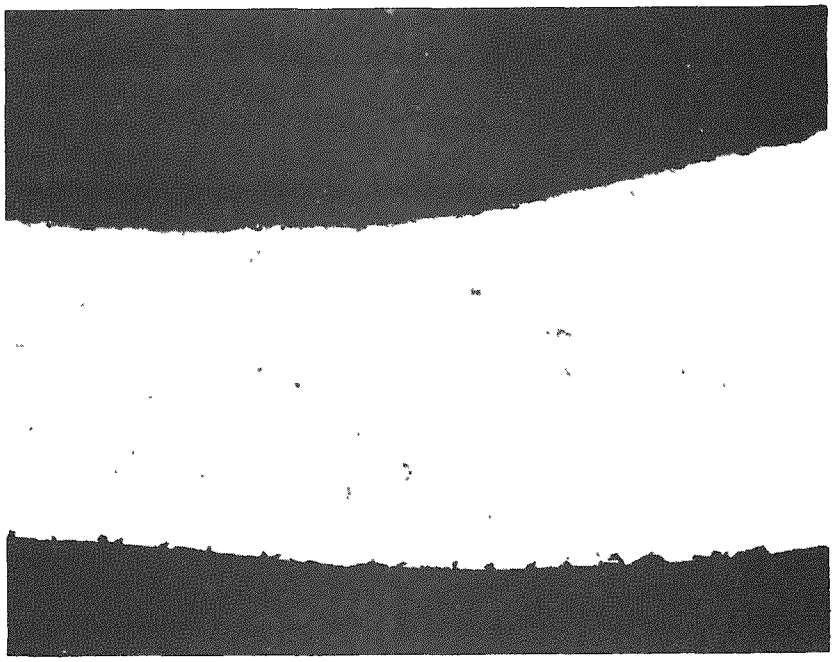
Two pieces of INOR-8, overlapped about 1/2 in. and welded, were exposed in the bottom of the container. The assembly showed no major attack at any area, including the crevice. Approximately one-fourth of one side was covered with a deposit of crystals of zirconium.

This dissolution experiment demonstrated the effectiveness of dissolving metal in retarding the corrosion of container materials. The reasons for such inhibition are not entirely clear, at present. Low corrosion rates were measured for both connected and insulated specimens; hence, inhibition cannot be ascribed entirely to galvanic protection unless, of course, the efficacy of the insulation was negated by the bridging of "snow" between the container and the specimen support. Other factors such as a lower flow rate of HF in the effluent, due to its consumption by the hydrofluorination of the Zircaloy-2, and a higher ratio of hydrogen to HF than had been studied previously, may have been equally important.

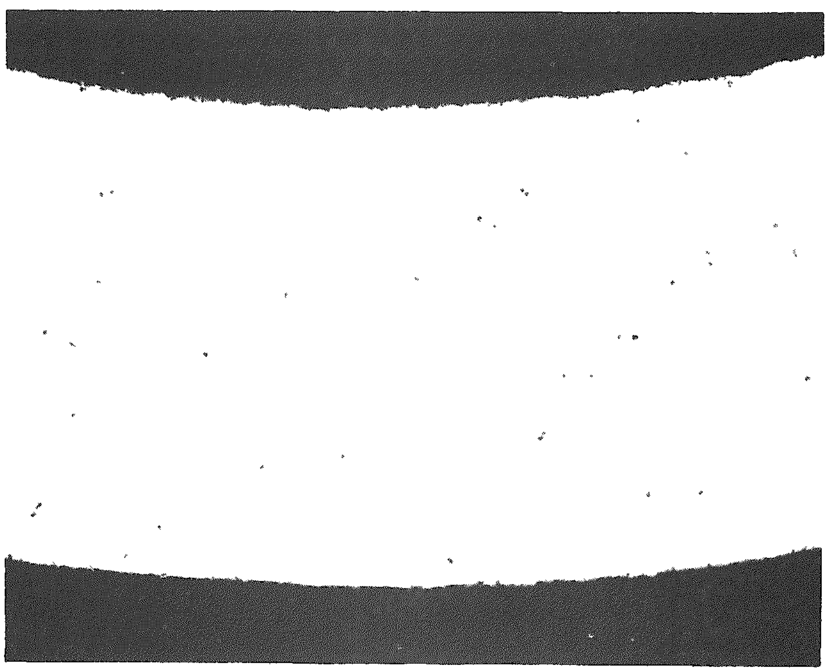
TABLE 2. CORROSION OF INOR-8 AFTER 214-HR EXPOSURE IN 700 C 43 MOLE PER CENT NaF-57 MOLE PER CENT LiF WITH DISSOLVING ZIRCALOY-2 (RUN 25)

Specimen	Penetration, mils per month: From Weight Loss	Penetration, mils per month: By Measurement[a] Micrometer	Penetration, mils per month: By Measurement[a] Metallographic	Visual Observations	Metallographic Observation
Coupon attached to insulated movable thermocouple well	0.7	1.7	2.6	Thin layer of metallic deposits on immersed portion; heavy etch at interface	No intergranular attack; moderately roughened surface
Insulated, movable, thermocouple well	--	31.	31.	Two loose clumps of crystals just above the interface revealed heavily etched depressions when removed; thin metallic deposits on immersed portion	Slight intergranular attack (about 1 mil deep) at several places plus moderately roughened surface on interface section
	--	0.5[b]	0.0[b]		No intergranular attack; slightly roughened surface on section 2 in. above bottom of tube (liquid phase)
Coupon attached to fixed sparge tube	0.2	0.7	--	Thin layer of metallic deposits on immersed portion	
Fixed sparge tube	--	0.0	--	Some metallic deposits on immersed portion; no apparent attack	
Straight coupon welded to movable tube	--	23.[c]	6.6[d]	Thin layer of metallic deposits on immersed portion; heavy etch at interface; micrometer rate of 23 is for reduction in width at necked-down edge	No intergranular attack; severely roughened surface
	--	0.9[e]	--		
Bent coupon welded to movable tube	--	2.6	--	Thin layer of metallic deposits on immersed portion; heavy etch at interface	
Movable tube	--	0.0	--	Exposed in vapor only; no apparent attack	
Welded piece exposed on the bottom of container	--	0.5	0.9	Approximately one-fourth of one side was covered with tightly adherent metallic-appearing crystals; spectrographic analysis indicated major constituent of crystals was zirconium with no tin present	No intergranular attack; no attack at the crevice; slightly roughened surface

(a) The micrometer and metallographic measurements were based on dimensional changes at sites of greatest attack, except as noted.
(b) Measured 2 in. below interface.
(c) Measured across width of specimen.
(d) Measured across thickness of specimen.
(e) Measured 0.4 in. below interface.



a. Interface, at Maximum Penetration

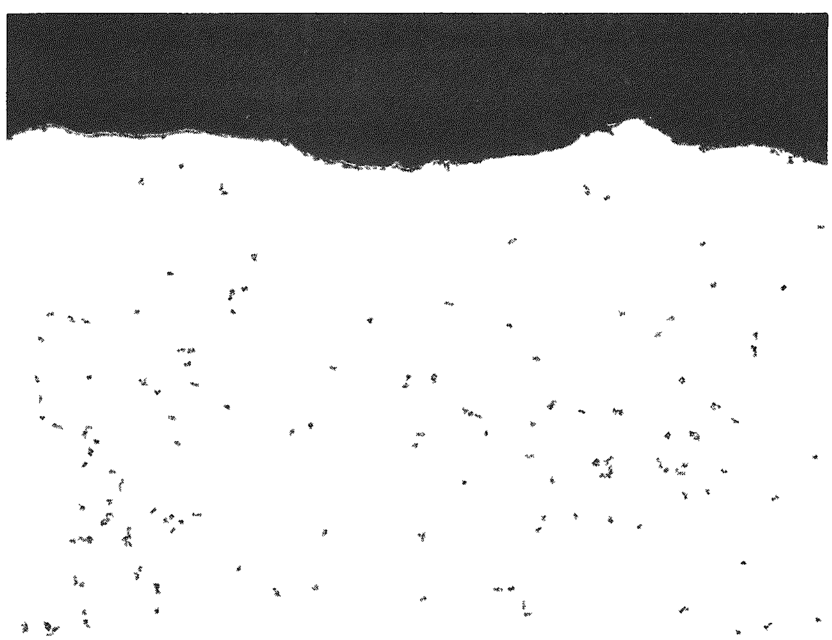


b. Liquid Portion, 2 In. From Bottom of the Well

FIGURE 20. ATTACK ON INOR-8 THERMOCOUPLE WELL IN RUN 25 WITH DISSOLVING ZIRCALOY-2 PRESENT IN THE SALT

100X C598

a. Movable, Insulated Coupon at the Interface



100X C603

b. Movable, Connected Coupon at the Interface

FIGURE 21. ATTACK ON TWO INOR-8 COUPONS IN RUN 25 WITH DISSOLVING ZIRCALOY-2 PRESENT IN THE SALT

CONCLUSIONS

The areas most susceptible to damage in containers holding molten salt are located at interface positions. Work has shown that rapid failure can be anticipated at such spots, particularly at high temperatures and in mixtures high in alkali metal salts. Preliminary results indicate that the corrosive attack can be retarded appreciably by maintaining dissolution of zirconium at all times. However, even under these conditions some selective attack was still observed.

INOR-8, INOR-1, and Hastelloy B have shown fairly good resistance to attack under the optimum conditions. However, Hastelloy B age hardens after prolonged use at the temperatures contemplated, and INOR-1 shows loss of molybdenum on unprotected outer surfaces. INOR-8 has been chosen as the most promising candidate material since it does not possess the above disadvantages and yet shows approximately the same resistance to corrosion as the other two alloys.

ACKNOWLEDGMENT

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PDM:CLP:OMS:EFS:FWF/mmk

APPENDIX

SUMMARY OF CORROSION AND ANALYTICAL DATA

APPENDIX

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Corrosion Results

The details of the operating conditions used with the Hastelloy B containers are summarized in Table A-1. Corrosion results for INOR-8, INOR-1, Hastelloy B, and silver are included in Table A-2.

Analytical Results

Salt Analyses

An analysis was made of each salt composition at the beginning and end of an experiment. Table A-3 summarizes the results obtained. The analyses were provided through the cooperation of ORNL chemists. It can be seen that, as might be expected, the major impurity in the salt from the Inconel containers (Runs 1 to 14) was chromium and the minor impurities were copper, iron, and nickel. In the Hastelloy B containers, the major impurity was nickel and smaller amounts of chromium, copper, iron, and molybdenum were found.

There is a fairly good correlation between the metal content of the salt and the corrosiveness of the exposure conditions as measured by the corrosion specimens. Longer exposure time increased the corrosion of the container as reflected in the salt analyses. More corrosive salt compositions showed higher metal pickup.

Some increase in sulfur content of the salt was noted with use.

Effluent-Gas Analysis

The amount of hydrogen present in the effluent gas should give some indication of the amount of corrosion taking place on the container walls and on the specimens. It was found that about 10 ml per hr of hydrogen was evolved when a Hastelloy B container was used and about seven times more was evolved when an Inconel container was used. Thus, in general, these results agree fairly well with the corrosion results obtained by other procedures.

HF Purity

One major impurity sometimes associated with liquefied HF is sulfur. It is believed that the sulfur canbe present as fluorosulfonic acid, as H_2S, or possibly as other compounds.

TABLE A-1. OPERATING CONDITIONS FOR CORROSION STUDIES IN HASTELLOY B CONTAINERS

Run	Nominal Salt Composition, mole per cent	Atmosphere, g per hr HF	Atmosphere, g per hr Hydrogen	Container	HF Tank	Temperature, C	Time, hr
17	59 NaF-41 ZrF_4	10	--	12-1	FC 11197	650	504
17 A	Salt remaining from Run 17	25	--	12-1	FC 11197	650	507
15	50 NaF-50 ZrF_4	10	--	11-1	B	650	500
15 A	Salt remaining from Run 15	10	--	11-1	B	650	510
16	50 NaF-50 ZrF_4	10	--	10-1	B	650	505
16 A	Salt remaining from Run 16	10	--	10-1	B	650	510
19	50 NaF-50 ZrF_4	10	0.24	11-2	FC 11197	650	425
19A[(a)]	Salt remaining from Run 19	10	--	11-2	FC 19874	650	479
19 B	Salt remaining from Run 19A	10	--	11-2	FC 19874	650	200
19 C	Salt remaining from Run 19B	10	--	11-2	FC 19874	700	200
22	44 NaF-56 ZrF_4-0.1 UF_4	10	0.24	15-1	FC 19874	650	199
22 A	Salt remaining from Run 22	10	--	15-1	FC 19874	650	200
20	47 NaF-53 LiF	10	--	13-1	FC 11197	700	263
21	45 NaF-55 LiF	10	0.24	14-1	FC 11197	700	123
24	43 NaF-57 LiF	10	--	12-2	FC 19874	700	93
18	19 NaF-55 ZrF_4-26 LiF-0.2 UF_4	Bad leak during nitrogen flush		10-2	None	600	22
23	19 NaF-55 ZrF_4-26 LiF-0.2 UF_4	10	--	16-1	FC 19874	600	200
23 A	Salt remaining from Run 23	10	--	16-1	FC 19874	650	200
23 B	Salt remaining from Run 23A	10	--	16-1	FC 19874	700	160
25[(b)]	43 NaF-57 LiF	10	--	14-2	FC 19874	700	214

(a) In Run 19 A, 20 ppm oxygen was added as air.
(b) Run 25 was conducted in presence of dissolving zirconium (Zircaloy-2).

TABLE A-2. CORROSION RESULTS FROM HYDROFLUORINATION RUNS MADE IN HASTELLOY B CONTAINERS

Run	Specimen Description: Material	Type	Position	Corrosion Rate Determined by Method Shown, mils per month: Weight Loss	Micrometer Measurement	Metallographic Section	Appearance After Exposure
17	INOR-8	Impingement tube	--	0.4	--	2.9	Light etch
	INOR-8	Coupon	Vapor	0.4	0.0	--	Ditto
	INOR-8	Coupon	Interface[(a)]	6.3	16	23	Necked down 11 mils at interface
	INOR-8	Coupon	Liquid	0.6	--	--	Black, rough surface
	INOR-1	Impingement tube	--	0.03	--	1.5	Very light etch
	INOR-1	Coupon	Vapor	0.4	0.0	--	Light etch
	INOR-1	Coupon	Interface	4.5	8.7	15	Necked down 6 mils at interface
	INOR-1	Coupon	Liquid[(a)]	2.5	--	--	Black, rough surface
	S-816	Coupon	Liquid[(a)]	3.4	10	12	Thickness reduced 14 mils
	Hastelloy B	Coupon	Interface	3.6	8.7	12	Necked down 6 mils at interface
17A	INOR-8	Impingement tube	--	2.2	--	--	Light etch
	INOR-8	Tube	Interface	15	45	--	Necked down 31 mils at interface
	INOR-8	Coupon	Vapor	0.25	--	--	Light etch
	INOR-8	Coupon	Interface	28	--	--	Severed at interface
	INOR-8	Coupon	Liquid	4.5	--	--	Moderate etch
	INOR-1	Impingement tube	--	0.1	--	--	Very light etch
	INOR-1	Tube	Interface	5.0	16	--	Necked down 11 mils at interface
	INOR-1	Coupon	Vapor	0.31	--	--	Moderate etch
	INOR-1	Coupon	Interface	20	--	--	Severed at interface
	INOR-1	Coupon	Liquid	7.9	--	--	Moderate to heavy etch
	Hastelloy B	Coupon	Interface	11.7	--	--	Severed at interface
	Hastelloy W	Tube	--	--	--	--	Ditto
15	INOR-8	Impingement tube	--	1.2	--	--	Light etch
15A	INOR-8	Impingement tube[(b)]	--	1.5	--	1.7	Heavy etch
	INOR-8	Tube	Vapor	0.5	--	1.4	Slight pitting; light etch
16	INOR-1	Impingement tube	--	2.1	--	--	Heavy etch
16A	INOR-1	Impingement tube[(b)]	--	1.7	--	5.2	Crystal deposits
	INOR-1	Tube	Vapor	1.5	--	3.9	Light etch
19	INOR-8	Impingement tube	--	0.09	--	2.2	Tarnish film
	INOR-8	Coupon	Vapor	0.35	--	--	Light etch
	INOR-8	Coupon	Interface	0.18	--	0.86	Ditto
	INOR-8	Coupon	Liquid	0.35	--	--	Ditto
	INOR-1	Impingement tube	--	0.003	--	0.86	Tarnish film
	INOR-1	Coupon	Vapor	0.11	--	--	Light etch
	INOR-1	Coupon	Interface	1.3	--	2.2	Ditto
	INOR-1	Coupon	Liquid	1.9	--	--	Moderate etch
	Hastelloy B	Coupon	Interface	0.8	--	--	Light to moderate etch

TABLE A-2. (Continued)

Run	Specimen Description: Material	Type	Position	Corrosion Rate Determined by Method Shown, mils per month: Weight Loss	Micrometer Measurement	Metallographic Section	Appearance After Exposure
19A	INOR-8	Impingement tube	--	1.5	--	--	Light etch
	INOR-8	Tube	Interface	3.5	--	--	Moderate etch
	INOR-8	Coupon	Vapor	0.36	--	--	Light etch
	INOR-8	Coupon	Interface	4.3	14	--	Necked down 9 mils at interface
	INOR-8	Coupon	Liquid	5.9	--	--	Moderate etch
	INOR-1	Impingement tube	--	1.0	--	--	Light etch
	INOR-1	Tube	Interface	4.2	6.7	--	Necked down 4.4 mils at interface
	INOR-1	Coupon	Vapor	0.34	--	--	Light etch
	INOR-1	Coupon	Interface	3.6	9.1	--	Necked down 6 mils at interface
	INOR-1	Coupon	Liquid	4.4	--	--	Metàllic deposits; moderate etch
	Hastelloy B	Coupon	Interface	1.2	--	--	Moderate etch
19B	INOR-8	Coupon	Interface	13	21	--	Necked down 5.8 mils at interface
	INOR-1	Impingement tube	--	0.42	--	--	Crystal deposits
	INOR-1	Coupon	Interface	17	38	--	Necked down 10 mils at interface
	Hastelloy B	Coupon	Interface	3.0	6.2	--	Necked down 1.7 mils at interface
19C	INOR-8	Impingement tube	--	5.7	--	--	Heavy etch
	INOR-8	Tube	Interface	Weight gain			Crystal deposits; light etch
	INOR-8	Coupon	Vapor	1.2	--	--	Ditto
	INOR-8	Coupon	Interface	29	--	--	Necked down at interface
	INOR-8	Coupon	Liquid	17	--	--	Heavy etch
	INOR-1	Impingement tube	--	3.4	--	--	Moderate etch
	INOR-1	Coupon	Vapor	0.76	--	--	Crystal deposits; light etch
	INOR-1	Coupon	Interface	21	--	--	Necked down at interface; crystal deposits
	INOR-1	Coupon	Liquid	17	--	--	Crystal deposits; heavy etch
	Hastelloy B	Coupon	Interface	14	--	--	Necked down at interface; crystal deposits
	Silver	Coupon	Interface	8.5	--	--	Necked down slightly at interface
22	INOR-8	Impingement tube	--	0.01	--	--	Tarnish film
	INOR-8	Coupon	Vapor	0.16	--	--	Ditto
	INOR-8	Coupon	Interface	0.39	--	2.9	Ditto, plus interface penetration of 0.8 mils
	INOR-8	Coupon	Liquid	0.84	--	--	Tarnish film
	INOR-1	Impingement tube	--	Weight gain			Ditto
	INOR-1	Tube	Interface	0.32	--	--	Ditto, plus some light etch
	INOR-1	Coupon	Vapor	0.08	--	--	Dark tarnish film
	INOR-1	Coupon	Interface	0.35	--	--	Ditto
	INOR-1	Coupon	Liquid	0.61	--	--	Ditto
	Hastelloy B	Coupon	Interface	0.26	--	--	Tarnish film

TABLE A-2. (Continued)

Run	Specimen Description: Material	Type	Position	Corrosion Rate Determined by Method Shown, mils per month: Weight Loss	Micrometer Measurement	Metallographic Section	Appearance After Exposure
22A	INOR-8	Coupon	Vapor	0.44	--	--	Some silver deposits, light etch
	INOR-8	Coupon	Interface	4.5	4.0	--	Loosely adherent dark powder; necked down 1.1 mils at interface
	INOR-8	Coupon	Liquid	3.7	--	--	Some silver deposits
	INOR-1	Impingement tube	--	0.63	--	--	Metallic coat plus crystal deposits
	INOR-1	Coupon	Vapor	0.34	--	--	Some silver deposits, light etch
	INOR-1	Coupon	Interface	3.6	4.0	--	Loosely adherent dark powder; necked down 1.1 mils at interface
	INOR-1	Coupon	Liquid	5.0	--	--	Moderate etch
	Hastelloy B	Coupon	Interface	2.6	5.1	--	Loosely adherent dark powder; necked down 1.4 mils at interface
	Silver	Coupon	Interface	6.5	58	--	Necked down 16 mils at interface
20	INOR-8	Impingement tube	--	9.0	--	--	Crystal deposits; heavy etch
	INOR-8	Tube	Interface	Severed		--	Severed at interface
	INOR-8	Coupon	Vapor	7.2	--	--	Heavy etch
	INOR-8	Coupon	Interface	Severed		--	Severed at interface
	INOR-8	Coupon	Liquid	20	--	28	Heavy etch
	INOR-1	Impingement tube	--	2.9	--	--	Numerous small pits; moderate etch
	INOR-1	Coupon	Vapor	1.7	--	--	Some severe etch
	INOR-1	Coupon	Interface	Severed			Severed at interface
	INOR-1	Coupon	Liquid	17	--	--	Moderate etch
	Hastelloy B	Coupon	Interface	Severed			Severed at interface
21	INOR-8	Impingement tube	--	--	--		Thick crystal deposits
	INOR-8	Tube	Interface	--	--		Heavy crystal deposit; heavy etch; attacked in liquid
	INOR-8	Coupon	Vapor	0.11	--	--	Light etch
	INOR-8	Coupon	Interface	--	--		Crystal deposits; heavy etch
	INOR-8	Coupon	Liquid	30	--	--	Heavy etch
	INOR-1	Impingement tube	--	--	--		Many loosely adherent crystal deposits; light etch
	INOR-1	Coupon	Vapor	0.02	--	--	Mottled tarnish film
	INOR-1	Coupon	Interface	Severed			Severed at interface
	INOR-1	Coupon	Liquid	--	--		Loosely adherent crystal deposits; heavy etch
	Hastelloy B	Coupon	Interface	Severed			Severed at interface
24	INOR-8	Impingement tube	--	18	--	--	Heavy etch
	INOR-8	Tube	Interface	48	--	--	Necked down at interface
	INOR-8	Coupon	Vapor	7.6	--	--	Crystal deposit; heavy etch
	INOR-8	Coupon	Interface	60	--	100	Necked down at interface
	INOR-8	Coupon	Liquid	43	--	--	Heavy etch
	INOR-1	Impingement tube	--	18	--	--	Crystal deposits; moderate etch
	INOR-1	Coupon	Vapor	13	--	--	Heavy etch
	INOR-1	Coupon	Interface	64	--	120	Necked down at interface
	INOR-1	Coupon	Liquid	38	--	--	Heavy etch

TABLE A-2. (Continued)

Run	Specimen Description: Material	Type	Position	Corrosion Rate Determined by Method Shown, mils per month: Weight Loss	Micrometer Measurement	Metallographic Section	Appearance After Exposure
23	INOR-8	Impingement tube	--	0.74	--	--	Light etch
	INOR-8	Coupon	Vapor	0.43	--	--	Ditto
	INOR-8	Coupon	Interface	1.0	--	--	Ditto
	INOR-8	Coupon	Liquid	2.5	--	--	Ditto
	INOR-1	Impingement tube	--	0.61	--	--	Ditto
	INOR-1	Coupon	Vapor	0.24	--	--	Ditto
	INOR-1	Coupon	Interface	0.76	--	--	Ditto
	INOR-1	Coupon	Liquid	1.7	--	--	Ditto
	Hastelloy B	Coupon	Interface	1.7	--	--	Ditto
23A	INOR-8	Impingement tube		0.63	--	--	Tarnish film
	INOR-8	Coupon	Vapor	1.1	--	--	Light etch
	INOR-8	Coupon	Interface	4.6	--	--	Moderate etch
	INOR-8	Coupon	Liquid	4.2	--	--	Ditto
	INOR-1	Impingement tube	--	0.23	--	--	Tarnish film
	INOR-1	Coupon	Vapor	0.55	--	--	Ditto, plus light etch
	INOR-1	Coupon	Interface	3.3	--	--	Moderate etch
	INOR-1	Coupon	Liquid	4.4	--	--	Ditto
	Hastelloy B	Coupon	Interface	2.1	--	--	Ditto
23B	INOR-8	Impingement tube	--	1.1	--	--	Light etch
	INOR-8	Coupon	Vapor	2.4	--	--	Ditto
	INOR-8	Coupon	Interface	13	20	--	Necked down 4.4 mils at interface
	INOR-8	Coupon	Liquid	15	--	--	Heavy etch
	INOR-1	Impingement tube	--	0.36	--	--	Some crystal deposits; light etch
	INOR-1	Coupon	Vapor	1.3	--	--	Light etch
	INOR-1	Coupon	Interface	13	22	--	Necked down 4.8 mils at interface
	INOR-1	Coupon	Liquid	11	--	--	Heavy etch
	Hastelloy B	Coupon	Interface	3.9	15	--	Necked down 3.2 mils at interface
25	INOR-8	Coupon	Interface, movable for constant interface position	--	23[(c)]	6.8[(d)]	Necked down 6.7 mils on one edge at interface; thin metallic coating on liquid portion
	INOR-8	Bent coupon	Interface, movable for constant interface position	--	2.7	--	Necked down 0.8 mil about 1-1/2 in. above interface; thin metallic coating on liquid portion
	INOR-8	Coupon	Interface, insulated, movable for constant interface position	0.73	1.7	2.7	Necked down 0.5 mil at interface; thin metallic coating on liquid portion
	INOR-8	Coupon	Interface, fixed position	0.15	0.68	--	Necked down 0.2 mil at one area; actual increase on other areas; thin metallic coating; light etch
	INOR-8	Tube	Thermocouple well, insulated	--	31	31	Localized attack about 9 mils deep near interface

(a) Support tube severed. Specimen remained in container during Run 17A. Thermocouple well and gas-inlet tube also severed.
(b) Total exposure was about 1000 hr since this tube was used in run above.
(c) Based on change in width.
(d) Based on change in thickness.

TABLE A-3. ANALYSIS OF SALT COMPOSITIONS

		Salt Analysis										
Run	Condition	Li, w/o	Na, w/o	Zr, w/o	F, w/o	U, w/o	Cr, ppm	Ni, ppm	Fe, ppm	Cu, ppm	Mo, ppm	S, ppm
1	Beginning	--	11.9	39.7	42.5	--	55	120	--	24	<10	24, 29, 27
2	Reused	--	--	--	--	--	--	--	--	--	--	--
3	Reused	--	--	--	--	--	--	--	--	--	--	--
	Final	--	13.3	41.5	45.4	--	5,835	655	1,300	--	--	--
4	Beginning	--	10.7	36.2	41.7	--	65	21	--	4	<10	17, 17, 22
	Final	--	--	--	--	--	--	--	--	--	--	69, 69
5	Beginning	--	12.8	39.4	44.8	--	55	80	--	23	<10	28, 51, 65
	Final	--	--	--	--	--	--	--	--	--	--	48, 44
6	Beginning	--	12.4	38.7	42.7	--	105	<10	--	28	<10	31, 37, 28
	Final	--	13.7	41.2	45.6	--	4,095	165	930	--	5	
7	Beginning	--	12.4	41.8	42.6	--	60	200	--	32	<1	35, 26, 28
	Final	--	13.8	41.2	45.7	--	4,930	135	--	--	--	
9	Beginning	--	11.4	43.5	45.4	--	145	110	200	--	--	6
11	Final	--	8.1	46.0	45.1	--	5,000	815	1,265	--	110	61, 50, 55
10	Beginning	--	13.8	41.2	45.7	--	4,930	135	--	--	--	--
	Final	--	14.3	38.1	44.3	--	23,500	850	4,760	--	2	90, 86, 81
12	Beginning	--	10.9	43.8	45.0	--	5	40	160	--	--	28, 35
	Final	--	8.8	43.5	43.8	--	20,800	16,800	460	--	10	33, 42
14	Final	--	11.4	43.5	44.8	--	4,400	1,095	1,970	--	8	121, 159, 125
17	Beginning	--	14.4	39.2	--	--	110	20	760	--	--	5
17A	Final	--	15.4	38.4	43.9	--	850	3,500	995	115	380	11, 10
15	Beginning	--	11.0	43.0	45.0	--	25	1	15	--	--	4
15A	Final	--	12.3	42.0	45.3	--	80	995	280	80	30	10, 10
16	Beginning	--	11.0	43.0	45.0	--	25	1	15	--	--	4
16A	Final	--	12.4	42.0	45.4	--	60	855	270	75	25	7, 7
19	Beginning	--	11.0	43.2	--	--	35	65	165	--	--	4
19A	Reused	--	11.7	42.6	44.2	--	226	1,400	425	40	24	16, 16
19B	Reused	--	--	--	--	--	--	--	--	--	--	--
19C	Reused	--	12.1	41.9	44.3	--	541	4,300	8,200	98	394	--
22	Beginning	--	8.95	46.0	--	0.107	6	20	150	--	--	3
22A	Reused	--	9.95	42.1	45.0	0.3	358	990	3,200	81	13	--
20	Beginning	11.0	32.0	--	--	--	30	10	45	--	--	8
	Final	10.0	26.6	--	52.3	--	700	42,500	4,200	905	12,400	--
21	Beginning	11.6	31.0	--	--	--	10	20	150	--	--	6
	Final	11.6	29.4	--	52.7	--	900	2,600	1,700	170	1,700	--
24	Beginning	9.7	33.8	--	55.4	--	40	270	310	--	--	5
	Final	10.7	29.0	0.14	53.8	--	1,300	25,000	18,000	<20	4,300	--
18	Beginning	2.28	32.0	46.2	--	0.69	10	45	205	--	--	5
23	Beginning	2.25	3.08	47.2	46.6	0.56	20	45	385	--	--	5
23A	Reused	--	--	--	--	--	--	--	--	--	--	--
23B	Reused	1.6	6.6	44.9	45.8	0.46	265	2,200	4,900	57	109	--
25	Beginning	9.1	36.1	--	54.4	--	25	60	185	--	--	5
	Final	4.3	12.4	32.6	49.8	--	528	<50	1,300	103	<10	--

To remove the more volatile impurities, about 3 lb of HF was bled from each tank prior to use in the experiments. Residual fractions were eliminated by not using further HF after the tank was approximately two-thirds depleted.

Table A-4 shows the sulfur content of the various tanks of HF used in the studies described earlier. According to G. I. Cathers of ORNL, the quantities present in all except Tank FC 19874 are low compared to normal commercial material.

The effectiveness of the nickel desulfurizer used in the corrosion assembly was evaluated by collecting samples at various locations in the system. It was found that the residence time in the desulfurizer was too short to effect appreciable removal of sulfur. However, some removal was obtained because several nickel tubes failed from attack by sulfur at the hottest area in the furnace.

Candidate Materials

Nine different metals or alloys were evaluated in the program.

Table A-5 gives the nominal analyses of the alloys most extensively studied. The INOR-8 alloys were from Heats SP-16, SP-19, M-1356, and 30-72. The specimens were usually given a heat treatment of 30 min at 1100 C under a hydrogen atmosphere. The INOR-1 alloys were from Heats Y-8195 and Y-8196. Most specimens were heated for 30 min at 925 C under hydrogen.

TABLE A-4. SULFUR CONTENT OF HF

Time of Sampling	HF Supply Cylinder	Point of Sampling	Sulfur in HF, ppm
After Run 12	A	From the tank	66
After Run 14	B	From the tank	86
After Run 14	B	Desulfurizer exit	101
During Run 14	B	Container exit	134
After Run 17A	FC 11197	From the tank	167
After Run 17A	FC 11197	Desulfurizer exit	143
During Run 17A	FC 11197	Container exit	172
After bleeding off first 3 lb of HF from new tank	FC 19874	From the tank	945

TABLE A-5. NOMINAL COMPOSITION OF ALLOYS EXPOSED

Alloy	Nominal Composition, w/o			
	Cr	Ni	Fe	Mo
INOR-8	7	71	5	16
INOR-1	-	78	-	20
Hastelloy B	-	65	5	28
Hastelloy W	6	62	6	25
Inconel	16	76	8	-