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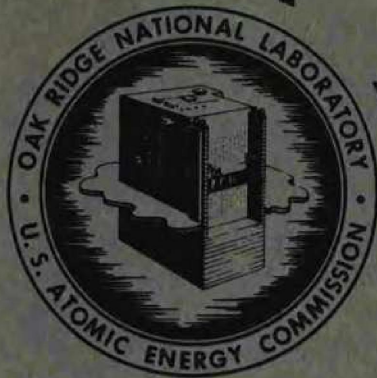Processes for Plutonium and Uranium

DISSOLUTION OF URANIUM-ZIRCONIUM

FUEL ELEMENTS IN FUSED NaF-ZrF$_4$

R. G. Wymer

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

DISSOLUTION OF URANIUM-ZIRCONIUM FUEL ELEMENTS

IN FUSED NaF-ZrF$_4$

R. G. Wymer

Technician: J. F. Land

DATE ISSUED

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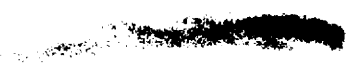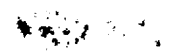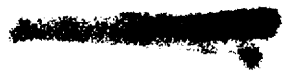
1.0 ABSTRACT

Further experiments confirmed previous indications that NaF-ZrF$_4$ is a satisfactory dissolvent for zirconium-uranium fuel elements. A very preliminary dissolution flowsheet, as a basis for a fused salt--fluoride volatility process, is presented.

2.0 INTRODUCTION

Dissolution in fused salt media of heterogeneous reactor fuels containing enriched uranium is economically attractive as a means of converting the uranium to a pure, easily recoverable form. Fluoride media are currently receiving attention, and STR fuel elements, whose principal constituent is zirconium, are particularly amenable to dissolution in fused salt media containing ZrF$_4$. Previous studies[1-5] have shown the feasibility of fused salt processing. The experiments reported here were carried out in order to obtain additional dissolution data needed for design of a tentative STR processing flowsheet. The results presented are very preliminary, and are based on only a few laboratory-scale experiments.

The author acknowledges the assistance received during the studies from G. R. Wilson and his group, of the Analytical Chemistry Division, who performed the many new and difficult chemical analyses which made this work possible, and of the late G. E. Klein of the Solid State Division, who made the x-ray analyses.

3.0 EXPERIMENTAL WORK

The equipment used in these studies (Fig. 1) consisted of a nickel dissolver vessel, an HF cold trap and wet test meter for measuring H_2 evolved, a voltage supply recorder for the metering equipment, and HF and N_2 gas metering equipment. In general, dissolution rates were determined both by H_2 evolution (as measured by the wet test meter) and by direct weighing of the specimens before and after their partial dissolution.

The initial dissolutions were made in a tubular dissolver (Fig. 2) in which the entire melt was agitated by the flowing gas. Reproducibility of data was very poor, and examination of the specimens after a dissolution run showed extreme inhomogeneity of attack. Attack was severe where the HF gas passed over the surface of the specimens, but was mild on the remainder of the surfaces. For later experiments, the dissolver was modified so that the entire specimen was contacted with HF gas as long as any gas was flowing to ensure greater dissolution uniformity. The modified dissolver (Fig. 3) was actually a lift pump, in which the gas, and therefore the melt agitation, was localized to a small region in the vicinity of the metal specimens. The fused salt was pumped up over the STR specimen by the pumping action of the HF gas, so that attack on the specimens was much more uniform. In spite of this, reproducibility of dissolution rate data was still poor. All dissolutions were made with the HF gas at atmospheric pressure, and 100 ml of fused salt was used in all runs.

In the lift-pump dissolver, effects due to HF alone cannot be differentiated from those due to HF dissolved in the fused salt. Studies on the mechanism of the reaction were therefore made in a U-tube dissolver (Fig. 4). In this dissolver an STR specimen can be
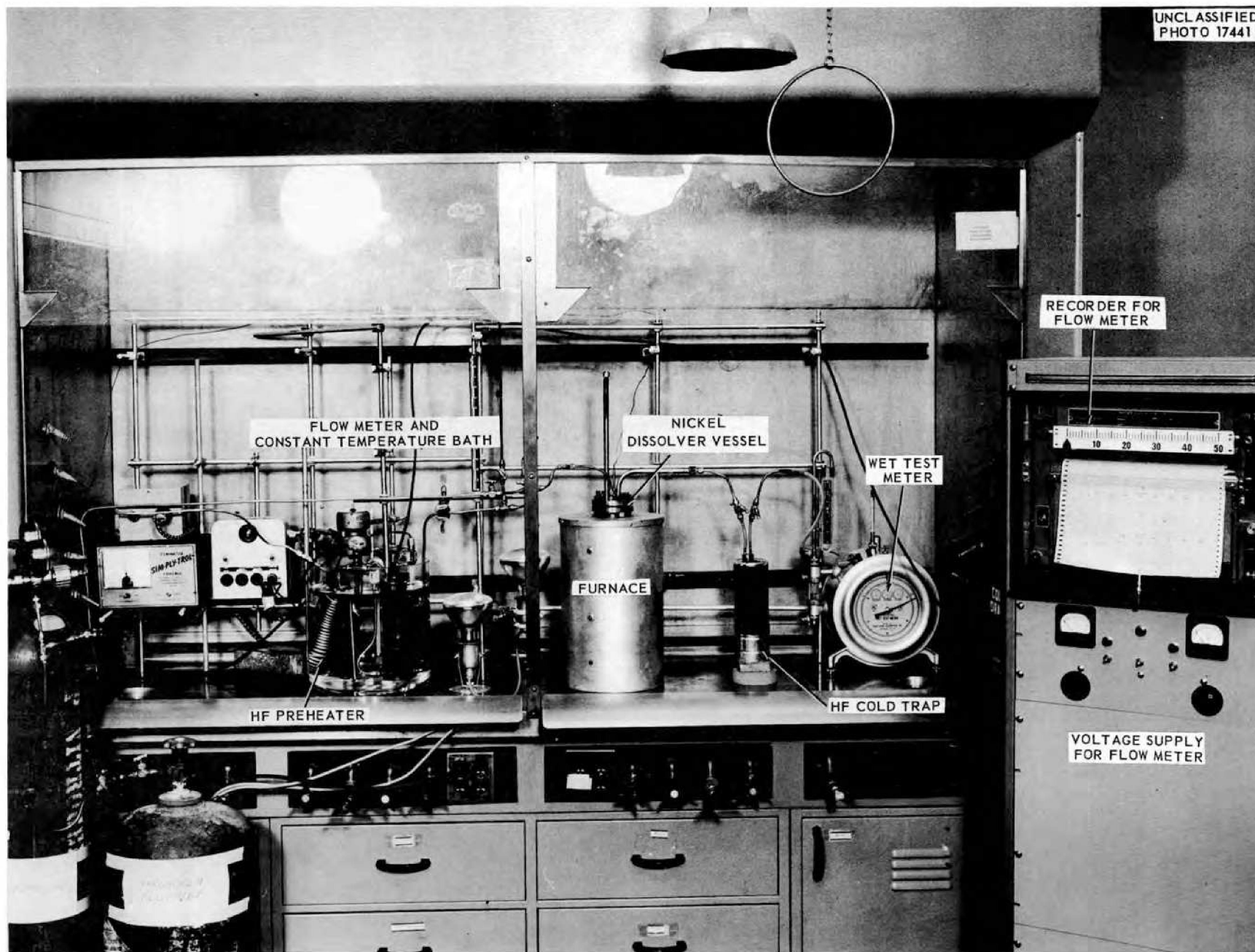
Fig. 1. Fused Salt Dissolution Equipment.

HF

¼-in. SWAGELOK FITTING FOR
REPLACEMENT OF INLET LINE

1-in. SWAGELOK FITTING ON
FILL PORT

½-in. TUBING WITH
FLARE FITTING

1-in. TUBING

THERMOCOUPLE
WELL

9-in. LENGTH OF 2-in.—
DIA TUBING

HF INLET TUBE, ¼-in.
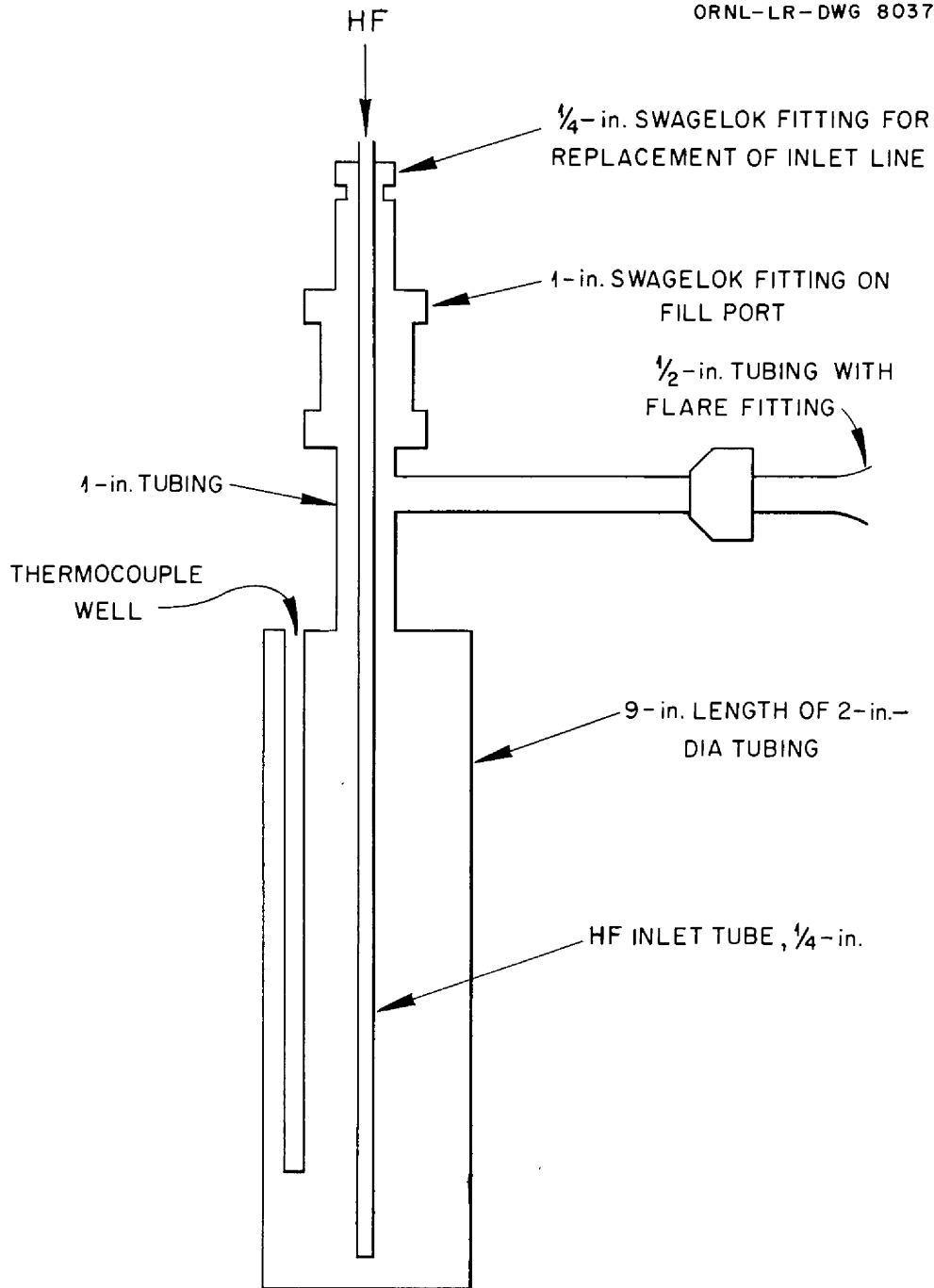
Fig. 2. Schematic Diagram of Reactor Used in Initial Dissolution Experiments.

HF Inlet

HF Outlet

Fused Salt

STR Specimen
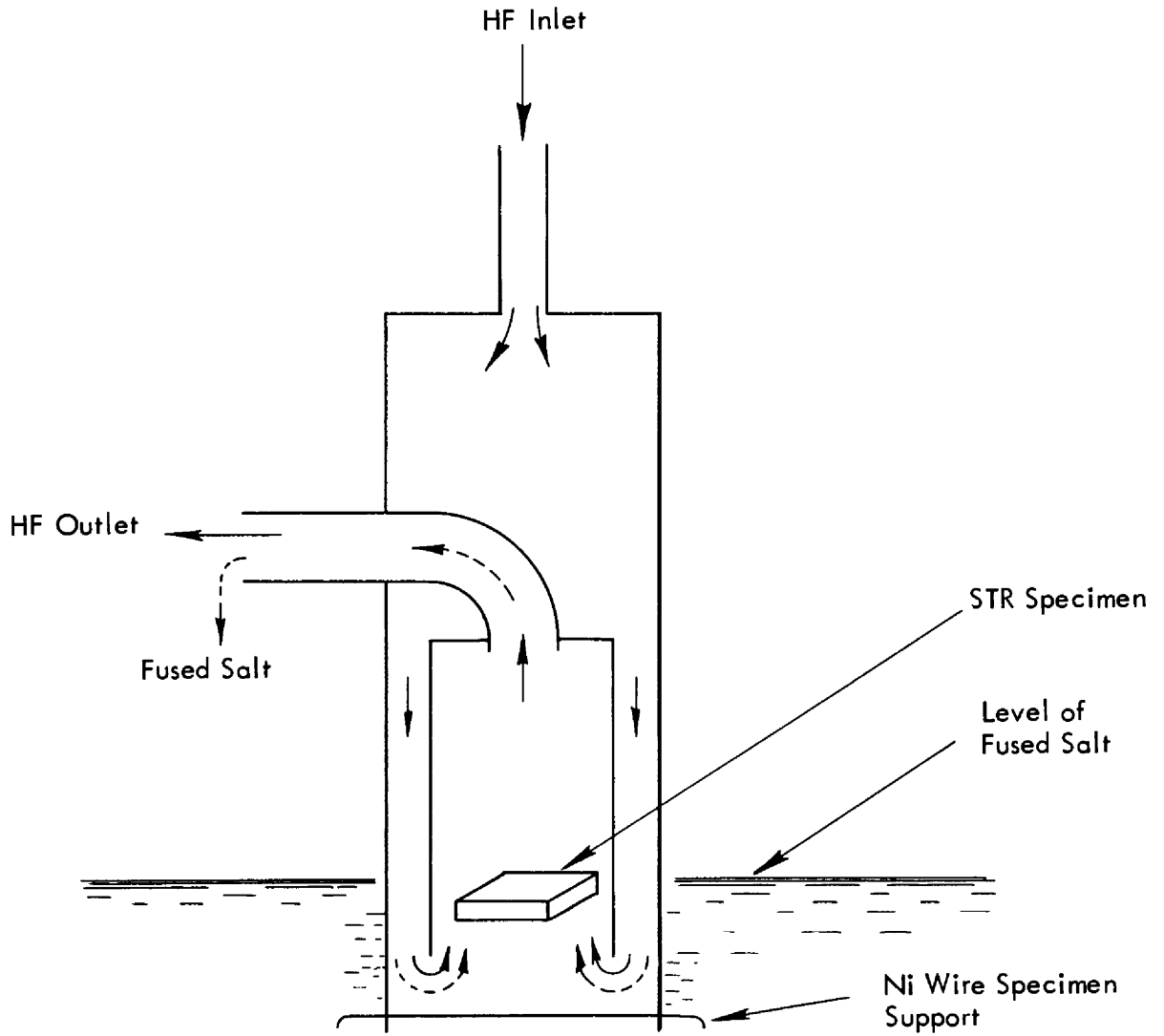
Level of
Fused Salt

Ni Wire Specimen
Support

Fig. 3. Schematic Drawing of HF Lift Pump Dissolver. The HF gas follows the
paths of the solid arrows and the fused salt, the broken arrows.
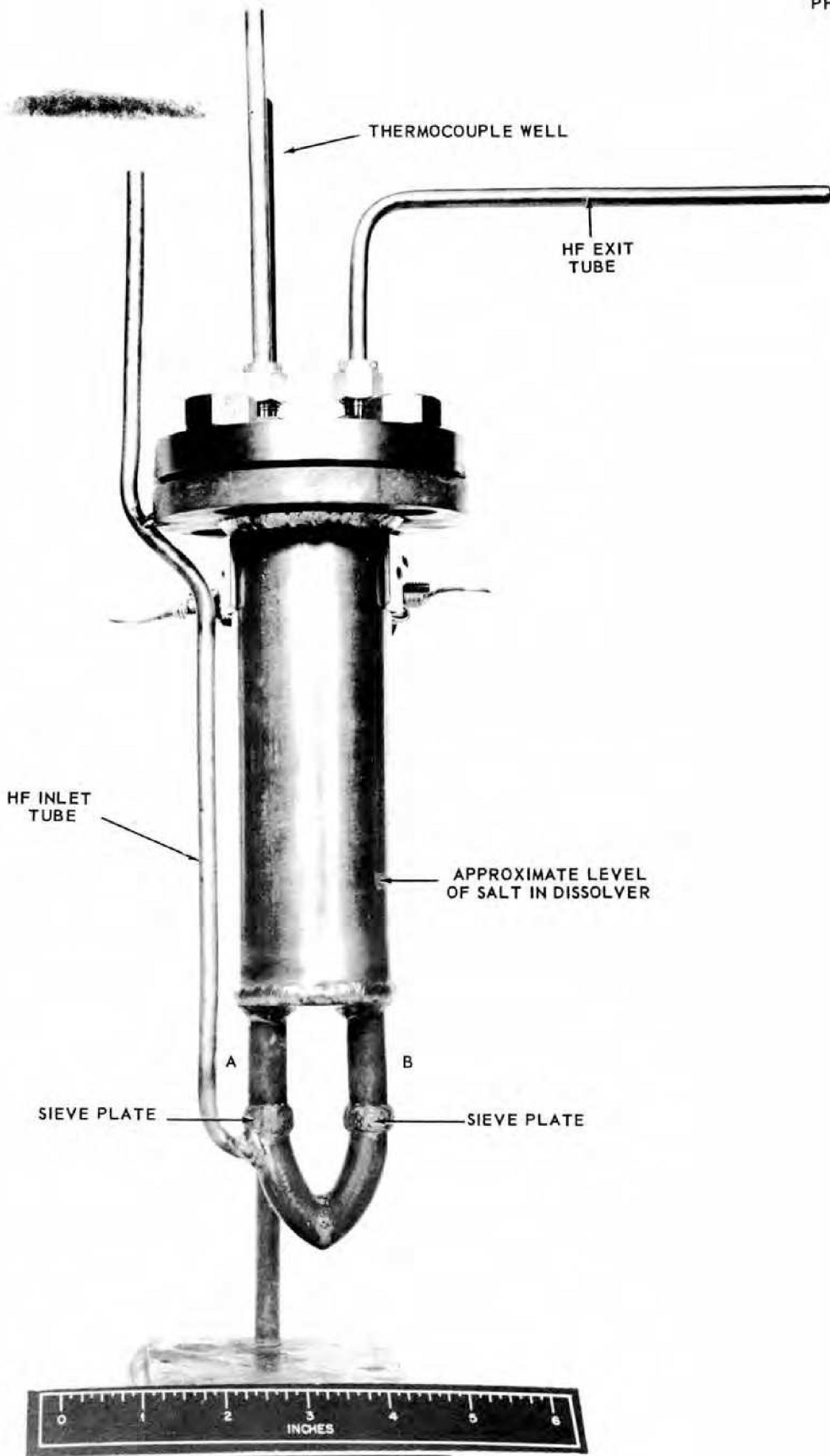
Fig. 4. U-Tube Dissolver.

placed in each of the arms, A and B, of the U tube attached to the bottom of the dissolver. The specimens rest on sieve plates. When HF gas is passed in through the inlet tube, it goes up through arm A, over the specimen on the sieve plate, rises through the salt in the main body of the dissolver, and passes out the HF exit tube. This sets up a salt-pumping action in arm A, which causes circulation of salt around the loop. At the same time, the fused salt becomes laden with dissolved HF. The specimen in arm B is thus exposed to salt containing dissolved HF but not to HF gas. The small diameter of arm A provides uniform gas coverage and dissolution, much as that achieved in the lift-pump dissolver. The auxiliary N_2 drying and deoxygenating equipment attached to the U tube for the experiments in which HF was replaced by nitrogen is shown in Fig. 5.

In order to avoid corrosion, insulation deterioration, and other problems associated with very high temperature processing of fluoride mixtures, $550^{\circ}C$ was set as the maximum melting point of the salt. This restricts the ZrF_4 content of the fluoride melt to the range 38-57 mole % (Fig. 6).

4.0 RESULTS

The dissolution rate of the simulated STR fuel element pieces was affected by the HF flow rate, temperature, and melt composition. Because of considerable scatter in the data, the results may be considered only as indicative of a trend. The nature of the metal did not affect the rate of dissolution, but did affect the type of attack by the reagent.

Effect of HF Flow Rate. At $700^{\circ}C$ the dissolution rate increased

VALVE

N$_2$

CaSO$_4$

H$_2$SO$_4$

TUBE FURNACE

COPPER TURNINGS AT 550°C

TO DISSOLVER

-8-
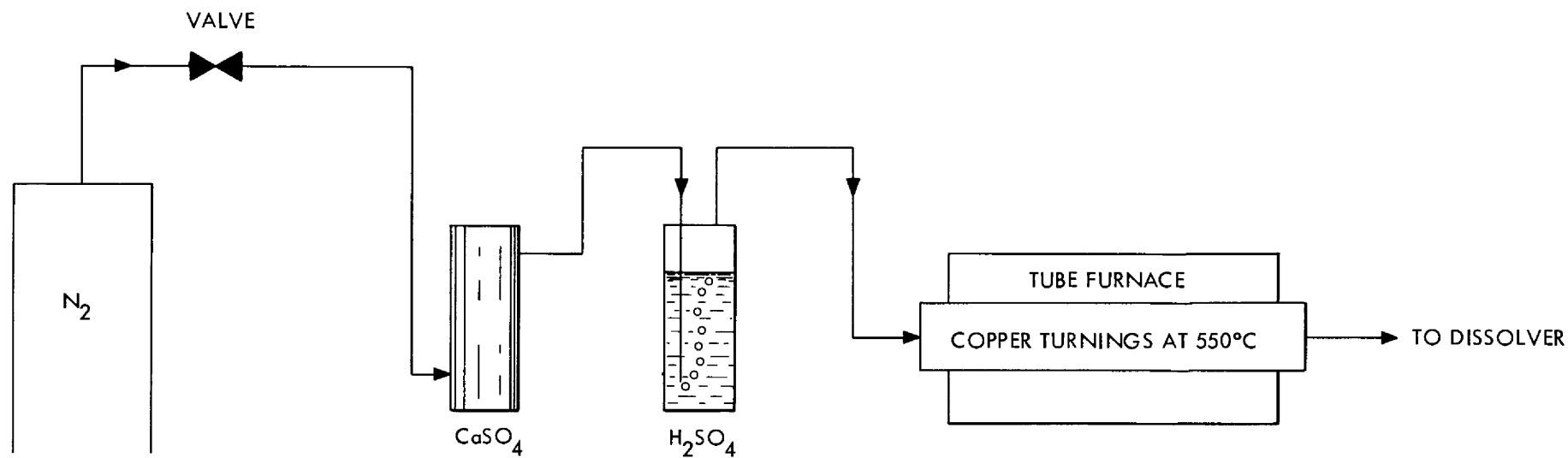
Fig. 5. Auxiliary N$_2$ Drying and Deoxygenating Equipment.
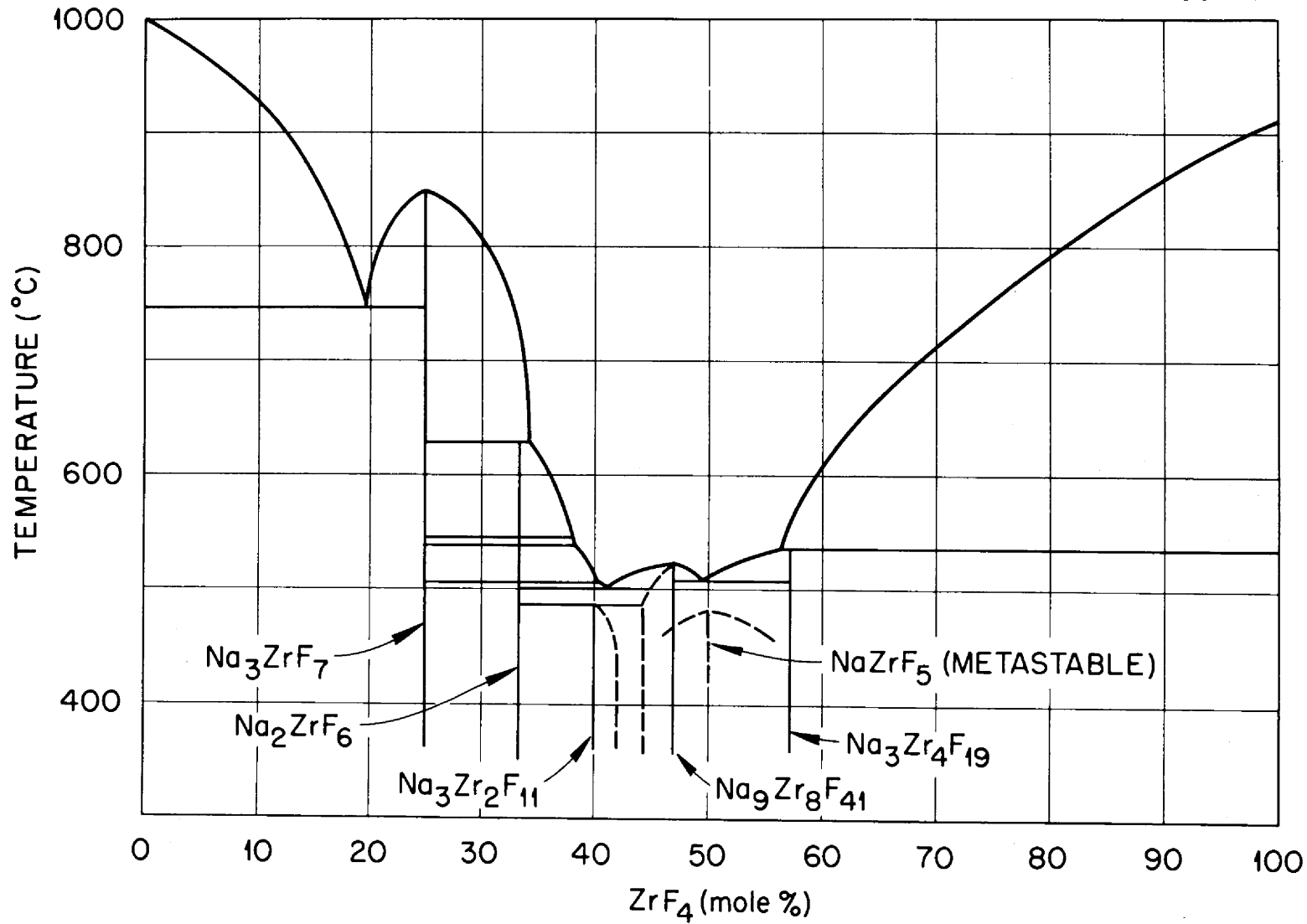
Fig. 6. The System NaF-ZrF$_4$.

with increasing HF flow rate (Fig. 7). There did not appear to be
any effect at 600°C, but at 800°C the rate increased and then de-
creased. In the preliminary studies in the ordinary dissolver, the
rate at 600°C increased with increasing HF flow rate (Table 1).
Comparison of results in the two dissolvers indicates a definite
dependence of dissolution rate on HF flow rate, even at 600°C, up to
a maximum value. It is assumed that this maximum value is reached
at or before an HF flow rate of 25 mg/min in the lift-pump dissolver,
where the excellent agitation leads to a high HF utilization
efficiency.

Table 1.   Dissolution Rates in Ordinary Dissolver

Conditions: 600°C; NaF/ZrF_4 = 1/1; atmospheric pressure;
              100 ml of melt

HF Flow Rate (mg/min)	Dissolution Rate $(mg/min/cm^2)$
25	0.58
40	0.50
50	0.74
83	1.1

The efficiency of HF utilization decreased rapidly with increasing
flow rate (Fig. 8). This factor affects the magnitude of the HF re-
cycle problem on a plant scale.

Effect of Temperature. At all HF flow rates tested, the disso-
lution rate increased with increasing temperature (Fig. 9). This
confirmed observations of other workers.[1,2]

Effect of Melt Composition. In the range 38 to 57 mole % ZrF_4
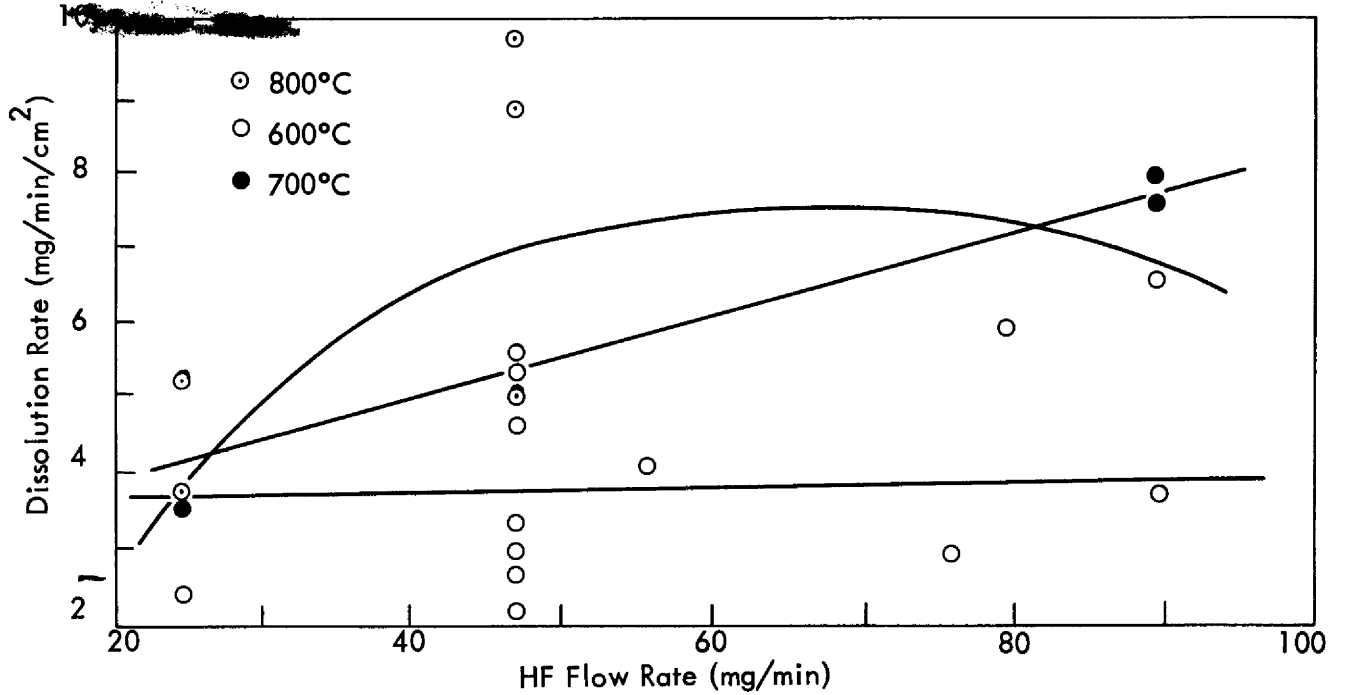
Fig. 7. Dissolution Rate of STR Specimens in 50-50 mole % NaF-ZrF$_4$ as a Function of HF Flow Rate.

Fig. 8. Utilization of HF as a Function of Flow Rate in Dissolution of STR Specimens in 50-50 mole % NaF-ZrF$_4$.

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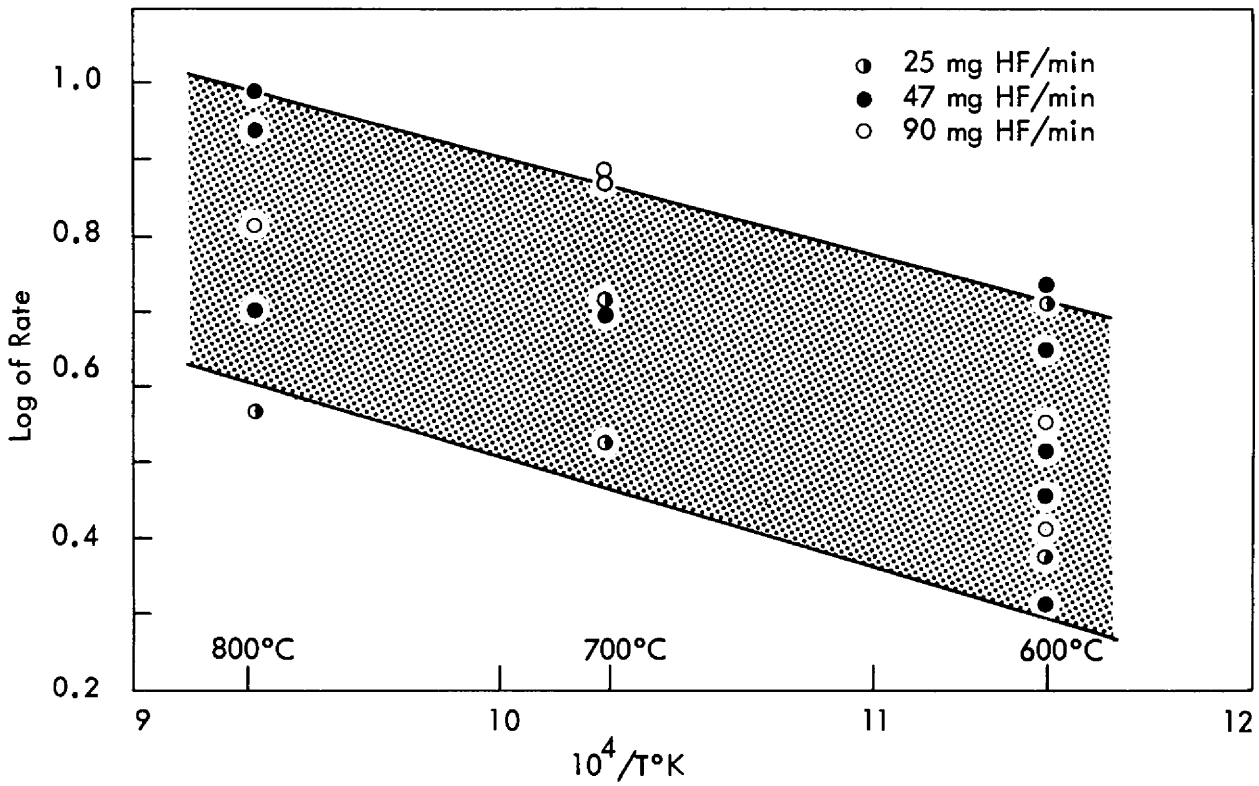
Fig. 9. Dissolution Rate of STR Specimens in 50-50 mole % NaF-ZrF$_4$ as a Function of Temperature.

the dissolution rate was considerably higher with the lower percentages of ZrF_4:
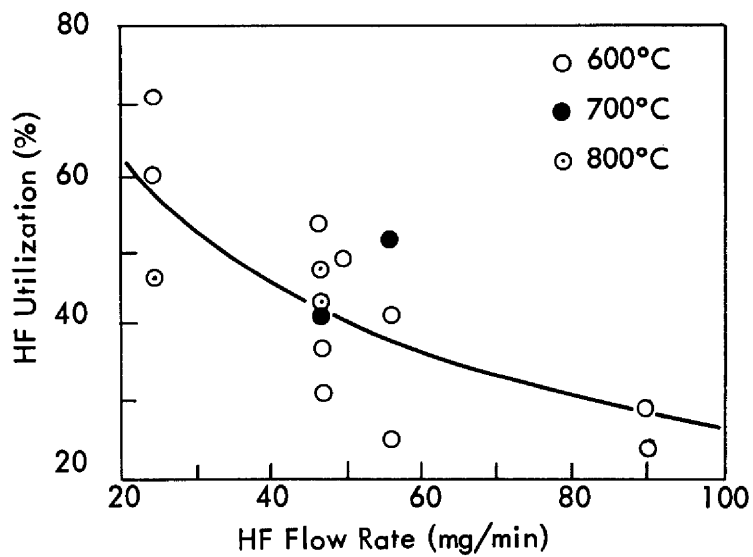
NaF/ZrF_4 mole ratio	Dissolution Rate (mg/min/cm^2)	
0.62/0.38	7.9 9.6 7.3	avg. = 8.3
0.43/0.57	1.0 0.8	avg. = 0.9

The dissolution rate in 50-50 mole % LiF-ZrF_4, which is about half as viscous as the comparable NaF-ZrF_4, was only 2.9 mg/min/cm^2. The dissolutions were made at 600°C, with an HF flow rate of 47 mg/min, at atmospheric pressure, in 100 ml of melt.

Effect of Nature of Metal. There was no significant difference between the dissolution rates of STR specimens, zircaloy-2, and crystal bar zirconium. There was a difference in the nature of the attack. With the STR specimens the attack on the core was greater than on the cladding (Fig. 10). With the zircaloy-2 specimens the attack along the upper edge was very regular (Fig. 11). With crystal bar zirconium there was extreme hydride formation, as indicated by myriad black areas suffusing the specimen (Fig. 12).

Nature of Product and Residue. After typical dissolution experiments, when the molten salt was poured onto a stainless steel pan it froze to a chalk-white solid. Invariably black particles 1 to 2 mm in diameter were distributed throughout the solid. X-ray analysis of the particles, which were picked out of the bulk of the salt, showed lines which could be taken as evidence for uranium metal, $ZrOF_2$, UO_2, ZrO_2, and UF_4. There were also lines for a metastable compound whose composition lay between $NaZrF_5$ and ZrF_4. It may be conjectured that the uranium metal was deposited from a fluoride of uranium in the melt by reduction by the more electropositive zirconium metal. The uranium would have been introduced

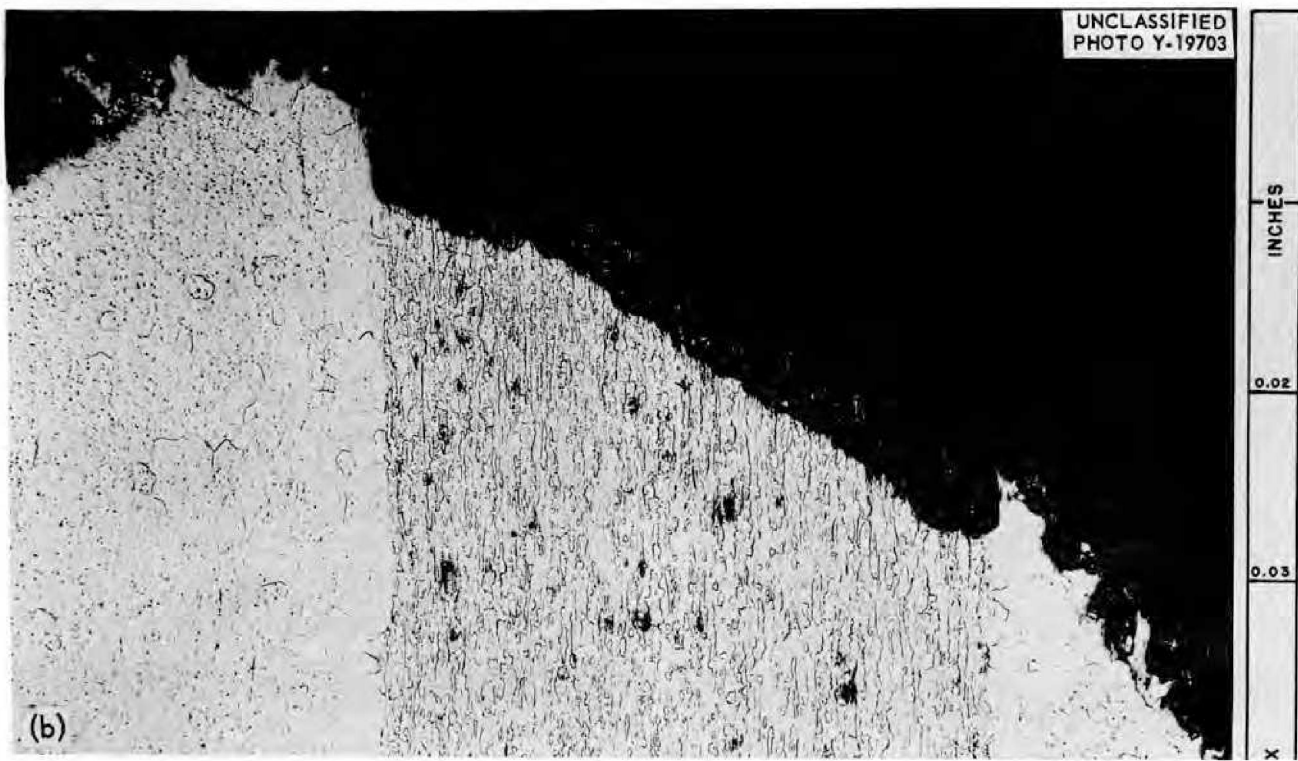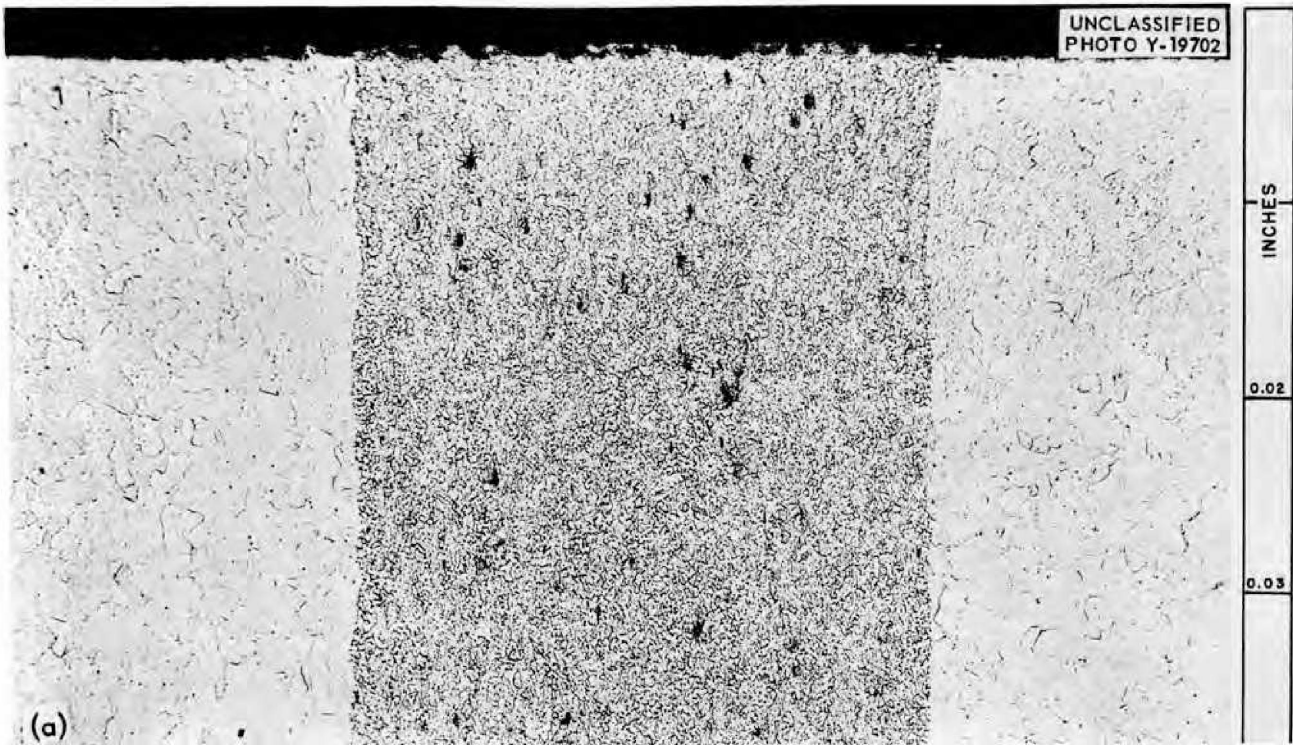Fig. 10. STR Fuel Plate. Bright field; 100X. (a) As received. (b) After dissolution treatment. (Confidential with caption)
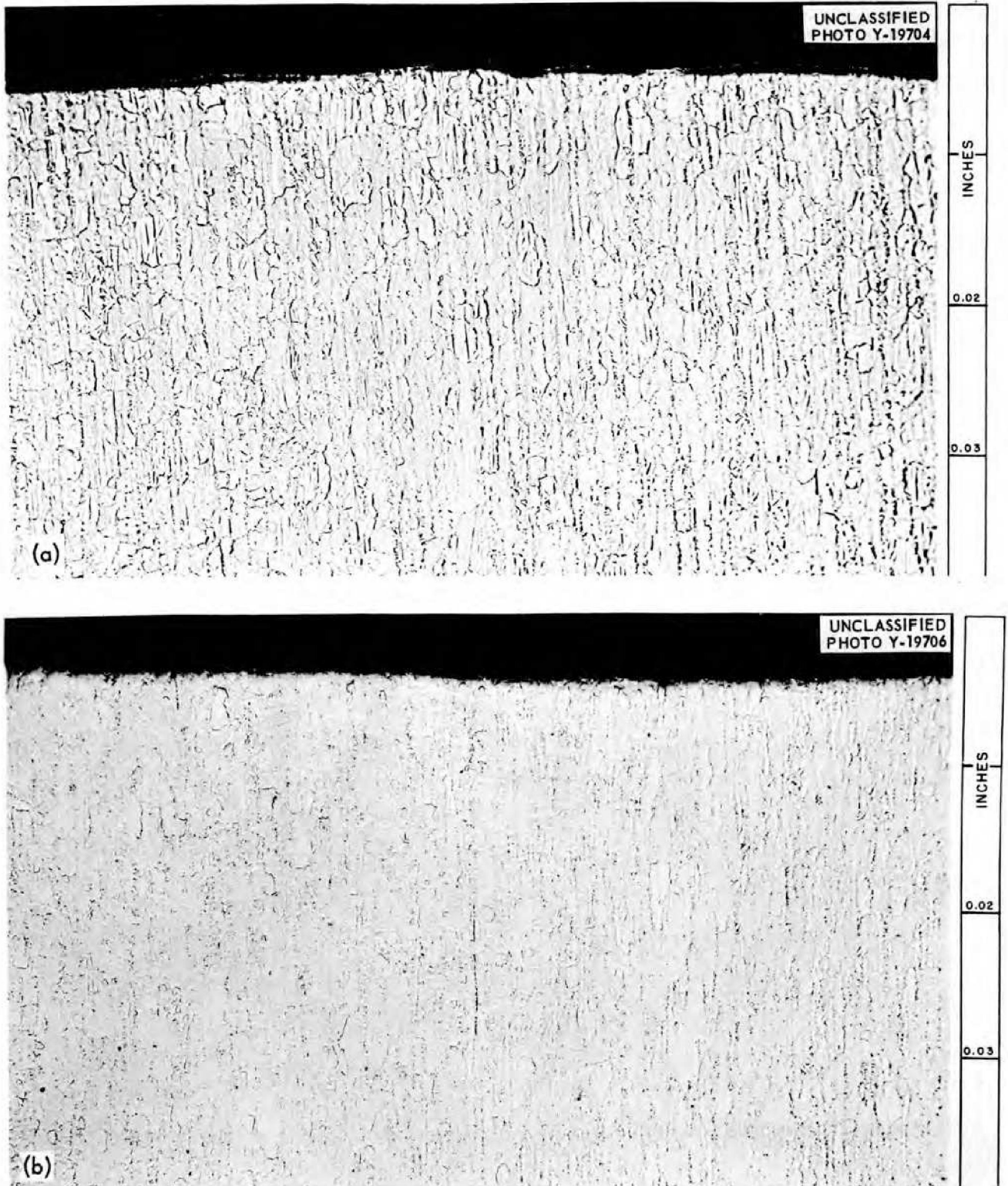
Fig. 11. Zircaloy-2. Bright field; 100X. (a) As received. (b) After dissolution treatment. (Confidential with caption)
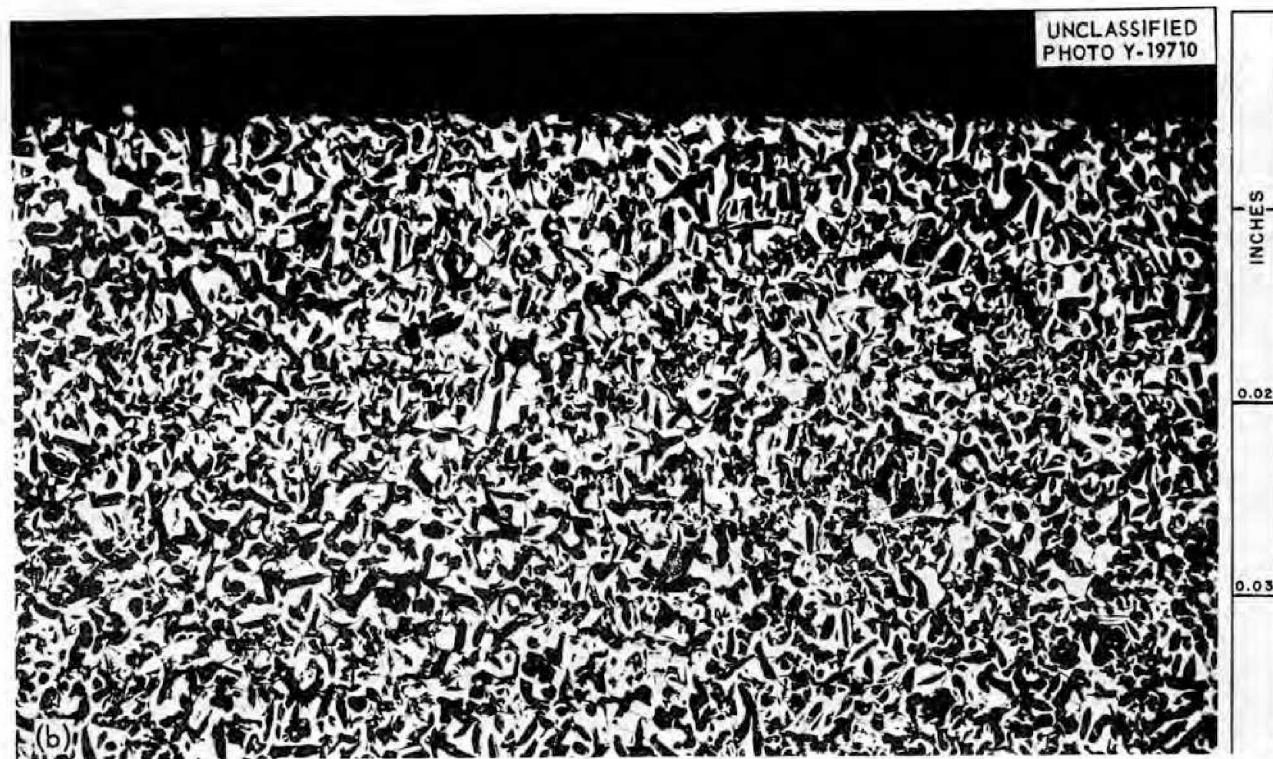
Fig. 12. Crystal Bar Zirconium. Bright field; 100X. (a) As received.
(b) After dissolution treatment. (Confidential with caption)

into the melt in the first place by dissolution out of that fraction of the core which was exposed along the edges of the STR specimens.

In general, the partially dissolved STR specimens were covered with a black adherent layer. When some of this layer was scraped off and analyzed by x-ray diffraction, lines attributable to UO_2 and zirconium metal were obtained.

5.0 DISSOLUTION MECHANISM

Little work has been reported so far that gives much insight into the details of the mechanism of dissolution. Results of a limited number of experiments designed to clarify this point indicated that the presence of HF is not necessary for dissolution.

The slight attack of STR fuel elements by HF gas alone is attributed to the presence of a protective coating of ZrF_4, which dissolves in the presence of fused salt and exposes more bare metal to the HF gas. However, in experiments in the U-tube dissolver (Fig. 5), there was no significant difference between the dissolution rate of STR specimens in fused salt containing dissolved HF with or without the flowing HF gas (Table 2). In the complete absence of HF, i.e., when the flowing HF gas was replaced by dry oxygen-free nitrogen, the rate of dissolution was still quite satisfactory (Table 3). Possible mechanisms in keeping with these results are pyrosol formation, as has been suggested[6] for dissolution of titanium in chloride melts, and reactions of the type

$$Zr^0 + 3Zr^{4+} \rightleftharpoons Zr^{3+} + 3Zr^{3+}$$

$$Zr^0 + Zr^{4+} \rightleftharpoons Zr^{2+} + Zr^{2+}$$
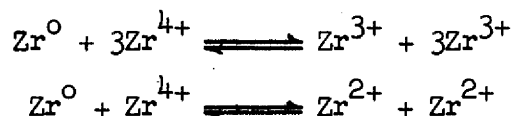
in which HF is not required for the primary disintegration step.

Table 2. Dissolution Rates of STR Specimens in Fused Salt
Containing Dissolved HF, with and without HF Gas

Conditions: $600^{\circ}C$; NaF/ZrF_4 = 1/1; atmospheric pressure

HF Flow Rate (mg/min)	Volume of Melt (ml)	Dissolution Rate (mg/min/cm^2)	
		In Salt	In Salt + Gas
25	75	2.2	2.6
56	75	3.0	2.8
47	100	5.1	4.2

Table 3. Dissolution of STR Specimens in Fused Salt
in Complete Absence of HF

Conditions: $600^{\circ}C$; NaF/ZrF_4 = 1/1; melts swept for 2 hr
with dry, oxygen-free nitrogen before specimens
lowered into it; 100 ml of melt

Duration of Run (min)	N$_2$ Flow Rate (arbitrary units)	Dissolution Rate (mg/min/cm^2)
42	12	1.4
52	---	1.1
120	42	0.4

Reducing Normality of Melts. Since STR specimens dissolve in
the absence of known oxidizing agents, the resulting melts should be
reducing in nature. The reducing normality of a 50-50 mole % NaF-
ZrF_4 melt was found to be of the order of 10^{-3} meq/g (Table 4). In
these experiments an ordinary dissolution was first performed, using
HF gas in the usual way. The melt was cooled under dried nitrogen
until it solidified, and was then transferred to a dry box where an

approximately 50-g sample was dug out. This sample was dissolved in 300 ml of solution* which was 1 $\underline{M}$ in $Al_2(SO_4)_3$, 1.5 $\underline{M}$ in H_2SO_4, and 0.017 $\underline{N}$ in $K_2Cr_2O_7$, and the amount of a standard reductant required for a back titration was compared with that required for a blank. In a second experiment, nitrogen was used instead of HF. In the third run nitrogen gas replaced the HF, but no STR specimen was used, so that any reducing normality present came from the melt itself, from dissolver vessel corrosion products, or from the nitrogen supply. Run 4 was a check made because a new supply of ZrF_4 salt for melts was obtained, and it was important to determine that no reducing impurity was introduced from this source. Run 5 was made with N_2 and no STR specimen, exactly as in runs 3 and 4, except that 1 wt % NiF_2 was added to see what effect the nickel salt would have on the reducing normality. Run 6 was a check for reducing impurities in the HF gas used.

There appeared to be an equilibrium between the oxidized and reducing forms of nickel. When 1 wt % NiF_2 was added to a typical melt, which contained 0.05 wt % NiF_2 initially, the reducing normality was doubled. The implication is that the nickel vessel wall enters into an equilibrium of the type $Ni + NiF_2 \rightleftharpoons 2NiF$. At $600°C$ the solubility of NiF_2 in a 50-50 mole % NaF/ZrF_4 melt is $\sim 0.4\%$. Therefore the NiF concentration in the postulated equilibrium is fixed when the NiF_2 is present in concentrations above 1 wt %, and vessel corrosion by NiF_2 is inhibited.

It is apparent that the zirconium which dissolves in the absence of HF gas is not a factor contributing to the reducing

---

* This solution must be heated to completely dissolve the $Al_2(SO_4)_3$, which reprecipitates on cooling. However, after the melt sample has been dissolved, sufficient complexing of aluminum ion with fluoride ion occurs that cooling without precipitation is possible. Auxiliary experiments showed such a solution to be an efficacious, rapid dissolvent for the melts, which are ordinarily very difficultly soluble.

normality. It may be supposed that the zirconium dissolves by pyrosol formation, but that the resulting dispersed metal is not oxidized by the dichromate-containing solution, and so is not measured in this way.

Table 4. Reducing Normalities of Various Melts

Conditions: $600^{\circ}C$; $NaF/ZrF_4 = 1/1$; 100 ml of melt; atmospheric pressure

Run	Gas	STR Specimen in Melt	NiF_2 in Melt (wt %)	Run Time (hr)	Dissolution Rate $(mg/min/cm^2)$	Reducing Normality of Melt (meq/g)
1	HF	Yes	~0.05	1	4.0	6.0×10^{-3}
2	N_2	Yes	~0.05	2	0.36	6.7×10^{-3}
3	N_2	No	~0.05	---	---	6.8×10^{-3}
4	N_2	No	~0.05	2	---	6.1×10^{-3}
5[a]	N_2	No	1	2	---	12.2×10^{-3}
6[b]	HF	No	1	1	---	8.6×10^{-3}

[a] 1 wt % NiF_2 was added to the melt.
[b] A different source of HF gas was used.

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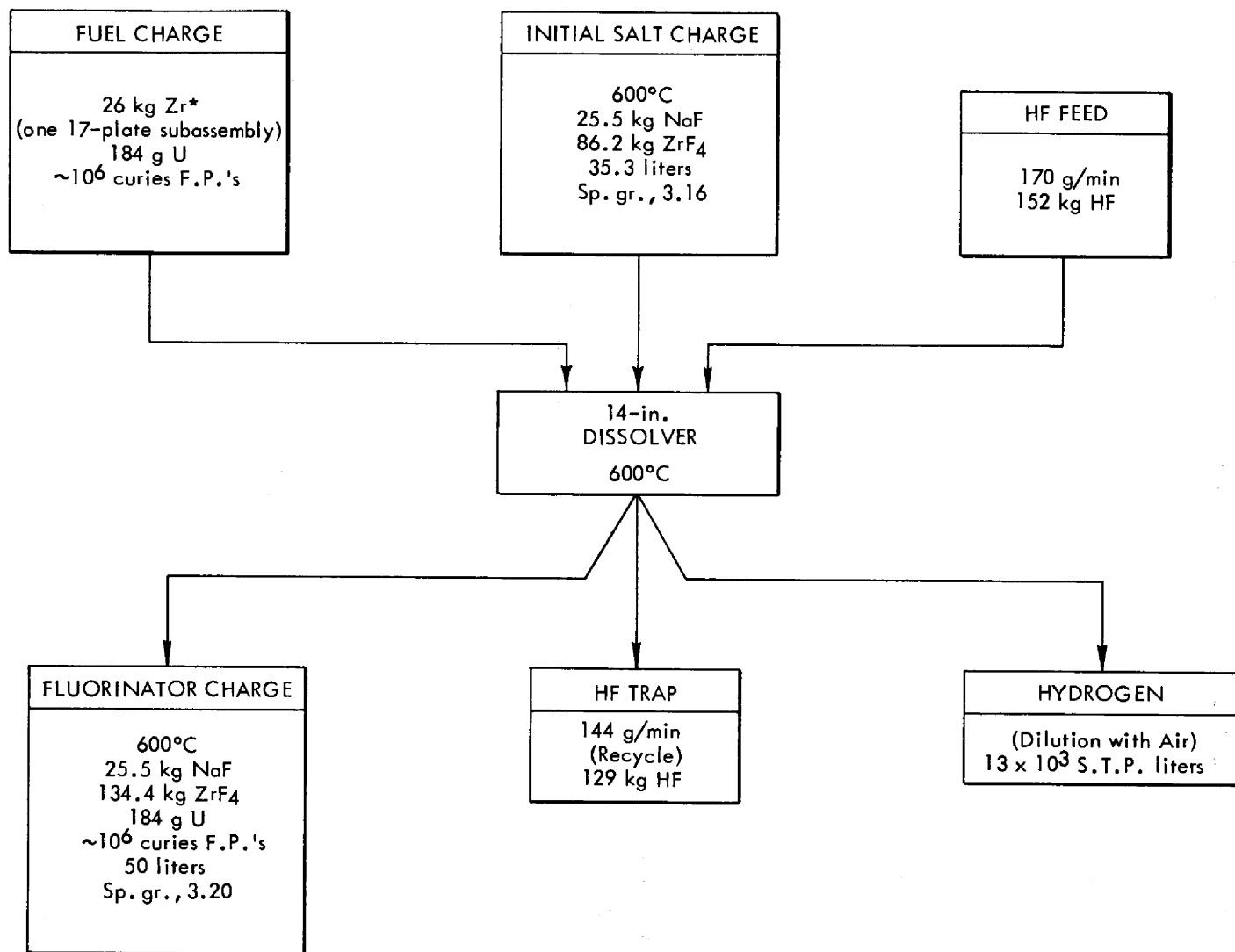
7.0 APPENDIX*

A tentative flowsheet for fused salt dissolutions was designed (Fig. 13). Since no engineering studies were made, this flowsheet is highly preliminary.

Size of Hydrofluorinator. The hydrofluorinator must be small enough in diameter that the initial salt charge covers the portion of subassembly charged. It must be large enough to accommodate the largest subassembly in less than half its diameter if a central HF pump is to be used (unless the assembly is put into the HF pump tube, as at ANL). Since the assemblies can be quartered, and may be handled in this way, the vessel must contain at least 12 in. of salt to cover such a portion. Subassemblies come with 5, 12, 14, and 17 fuel plates. Since each subassembly has two side plates, there are 7, 14, 16, and 19 plates, respectively, in these subassemblies. The edges of the plates are 6 mm thick, so the thickest subassembly is about $0.6 \times 19 = 11.4$ cm, or 4.5 in., thick. A 12-in.-i.d. dissolver would thus allow enough room for a 3-in.-o.d. HF pump, and a 14-in.-i.d. tank would allow enough for a 5-in.-o.d. HF pump, if such a device was used.

A salt charge to the hydrofluorinator should be sufficient to process as much as one complete 17-fuel-plate subassembly on the one hand, or as little as one complete 12-plate subassembly on the other. These are the charge limits which may be met in operation (Table 5). Thus, the total weight of zirconium to be dissolved ranges from $16 \times 1.23 = 19.7$ kg to $21 \times 1.23 = 25.8$ kg. These values may be rounded off to 20-26 kg of zirconium.

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* This appendix originally published as CF-56-5-19.

FUEL CHARGE

26 kg Zr*
(one 17-plate subassembly)
184 g U
~10^6 curies F.P.'s

INITIAL SALT CHARGE

600°C
25.5 kg NaF
86.2 kg ZrF$_4$
35.3 liters
Sp. gr., 3.16

HF FEED

170 g/min
152 kg HF

14-in.
DISSOLVER
600°C

FLUORINATOR CHARGE

600°C
25.5 kg NaF
134.4 kg ZrF$_4$
184 g U
~10^6 curies F.P.'s
50 liters
Sp. gr., 3.20

HF TRAP

144 g/min
(Recycle)
129 kg HF

HYDROGEN

(Dilution with Air)
13×10^3 S.T.P. liters

*To be added one-quarter of a subassembly at a time.

Fig. 13. Tentative Flowsheet for Fused Salt Dissolution. Dissolution time: approximately 15 hr.

Table 5. <u>Number of Fuel Plates in a Hydrofluorinator Charge</u>

No. of Fuel Plates in Subassembly	No. of Subassemblies per Batch	Total No. of Plates[a]
5	2	18
12	1	16
14	1	18
17	1	21

[a]The end plates are twice as thick as the fuel plates; they contain twice the amount of zirconium, and each is counted twice.

Setting 50 liters as the approximate volume desired for subsequent use in the fluorination, we may calculate the initial amount of salts to be charged to the hydrofluorinator. The density of a 57 mole % ZrF_4-43 mole % NaF melt at $600^\circ C$ is 3.2.* Therefore, 50 liters contains 50 x 3.2 = 160 kg of salt, or

$$\text{kg NaF} = \frac{160 \times \dfrac{42 \times 0.43}{167 \times 0.57}}{1 + \dfrac{42 \times 0.43}{167 \times 0.57}} = \frac{30.4}{1 + 0.190} = 25.5$$

$$\text{kg ZrF}_4 = \frac{160 \times \dfrac{0.57 \times 167}{0.43 \times 42}}{1 + \dfrac{167 \times 0.57}{42 \times 0.43}} = \frac{5.28 \times 160}{1 + 5.28} = 134.4$$

From this, it follows that the weight of zirconium present is 134 x 91.2/167 = 73.2 kg. Subtracting this from 26 kg, which is the most zirconium to be dissolved in a single melt, we arrive at a value of approximately 47 kg of zirconium, which is the least amount with which we may start in the melt. This leads to an initial melt of 25.5 kg of

* Interpolated from data given in Ref. 2.

NaF and $47 \times 169/91.2 = 86.2$ kg of ZrF_4. The composition is 45.9% ZrF_4--54.1% NaF. At $600^{\circ}C$ the density of such a melt is 3.16 g/cc, so the volume, V, is $(25.5 + 86.2)$ 3.16 = 35.3 liters. In a 12-in.-dia hydrofluorinator this would mean a depth of 19.0 in. of salt; in a 14-in.-dia hydrofluorinator it would mean a depth of 14 in. of salt. Both these values exceed the minimum requirement of 12 in. of depth. For increased capacity and freeboard space, a 14-in.-dia dissolver is recommended.

The following equation is useful in making calculations of the weight of one of the salts in a system when the mole fractions and total salt weight are known:

$$W_1 = \frac{T}{1 + \frac{M_2 F_2}{M_1 F_1}}$$

where W_1 = weight of salt of interest

$\qquad F_1$ = mole fraction of salt of interest

$\qquad M_1$ = molecular weight of salt of interest

$\qquad F_2$ = mole fraction of second salt

$\qquad M_2$ = molecular weight of second salt

$\qquad T$ = total weight of combined salts

Calculation of Hydrogen Fluoride Requirements. If the fused melt is well agitated, dissolution rates of 2-5 $mg/min/cm^2$ may be expected. A value of 3 $mg/min/cm^2$ has been selected for these calculations.

Consideration of the physical construction of the fuel assemblies leads to the conclusion that a thickness of 0.65 cm must be dissolved to produce a melt practically free of metal. (In practice, unavoidable dissolution heterogeneities will be experienced, and additional dissolution time beyond that required to dissolve a thickness of 0.65 cm will be necessary to ensure that no pieces of metal remain.) The uranium-containing portions of the fuel assemblies are only 0.3 cm

thick; therefore complete dissolution of the twice-as-thick edge portions will ensure that the uranium-containing part has completely dissolved.

Taking the dissolution rate of 3 mg/min/cm^2, and half of 0.65 cm, or 0.33 cm, as the maximum distance which must be penetrated (since dissolution takes place on both sides of the 0.65-cm-thick edge), a value of $0.33 \times 6.4/0.003 \times 60 = 12$ hr is obtained for the time required for complete dissolution. If 26 kg of zirconium is to be dissolved, then $26,000 \times 4/91.2 = 1140$ moles of hydrogen fluoride will be used, assuming 100% efficiency of utilization. This corresponds to a hydrogen fluoride flow rate of $1140 \times 20/12 \times 60 \times 43 = 0.74$ mg/min/ml. While it is not a valid procedure to attempt to compare hydrogen fluoride flow rates on the basis of volumes of hydrogen fluoride passed into a fixed volume of salt in a given time when other scale-up factors are not comparable, it is the best method at hand. On the basis of such a comparison, a hydrogen fluoride utilization efficiency of about 30% may be estimated. This means, however, that $3 \times 1140 = 3420$ moles of hydrogen fluoride is required, which in turn increases the flow rate to $3 \times 0.74 = 2.2$ mg/min/ml, at which rate only about 15% hydrogen fluoride utilization may be expected. Finally, therefore, an approximate value of $1140/0.15 = 7600$ moles of hydrogen fluoride required to dissolved 26 kg of zirconium is obtained. This means that $7600-1140 = 6460$ moles of hydrogen fluoride must be recycled in what may be a somewhat radioactive operation as volatile fluorides (such as ZrF_4, MoF_6, NbF_5) accumulate.

In order to ensure that no metal remains, a dissolution time of 15 hr would be desirable. Therefore, a hydrogen fluoride flow rate to the dissolver of $7600 \times 20/15 \times 60 = 170$ g/min is required, and of this $0.85 \times 170 = 144$ g/min must be trapped for recycle.