ORNL-1885(Del.)

Contract No. W-7405, eng 26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

A FUSED SALT—FLUORIDE VOLATILITY PROCESS FOR RECOVERY AND DECONTAMINATION OF URANIUM

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DELETED VERSION

Classification changed to UNCLASSIFIED
by authority of J A Ruff 2-28-57
by H Knied date 1-23-12
and CM Davenport date 1-24-12

DATE ISSUED:
OCT 10 1955

Photostat Price $4.80
Microfilm Price $2.70

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Department of Commerce
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0.0 ABSTRACT

A preliminary chemical flowsheet is presented of a fluoride volatility process for recovering and decontaminating uranium from heterogeneous reactor fuels after dissolution in a fused salt. In laboratory work, a gross β decontamination factor of $>10^4$ was obtained in the fluorination of a UF_4-NaF-ZrF_4 melt by passing the product UF_6 through NaF at 650°C. The solubility of UF_6 in molten NaF-ZrF_4 was shown in kinetic studies to cause a lag in the evolution of UF_6 from the fluorinator. Corrosion of nickel in the fluorination step appeared to be 2-4 mils/hr during the time that uranium was present. The average corrosion rate over the process as a whole was less than 0.4 mil/hr. Earlier studies were reported in ORNL-1709 and 1877.

1.0 FLOWSHEET

A proposed method (see Fig. 1) of recovering and decontaminating uranium from heterogeneous reactor fuels consists in dissolution in a molten salt of the type NaF-ZrF_4 in the presence of HF and conversion of the UF_4 thus formed to UF_6 by means of F_2. More than 99.9% of the uranium is recovered by sparging the UF_6 from the solution with excess F_2, with a gross β decontamination factor of 100-300 for long-decayed uranium. The decontamination factor with respect to nonvolatile fission product activity and neutron poisons is in the range 10^4-10^6. The effluent UF_6 is passed through a sodium fluoride bed at 650°C, which absorbs much of the ruthenium and niobium fluorides, to give an over-all decontamination factor of $>10^4$. If the UF_6 is to be used to make fluoride reactor fuel, it can be reduced to UF_4 and used without further decontamination. If it is to be used in a gaseous diffusion plant or is to be reduced to uranium metal for refabrication of fuel elements, more decontamination will be necessary.

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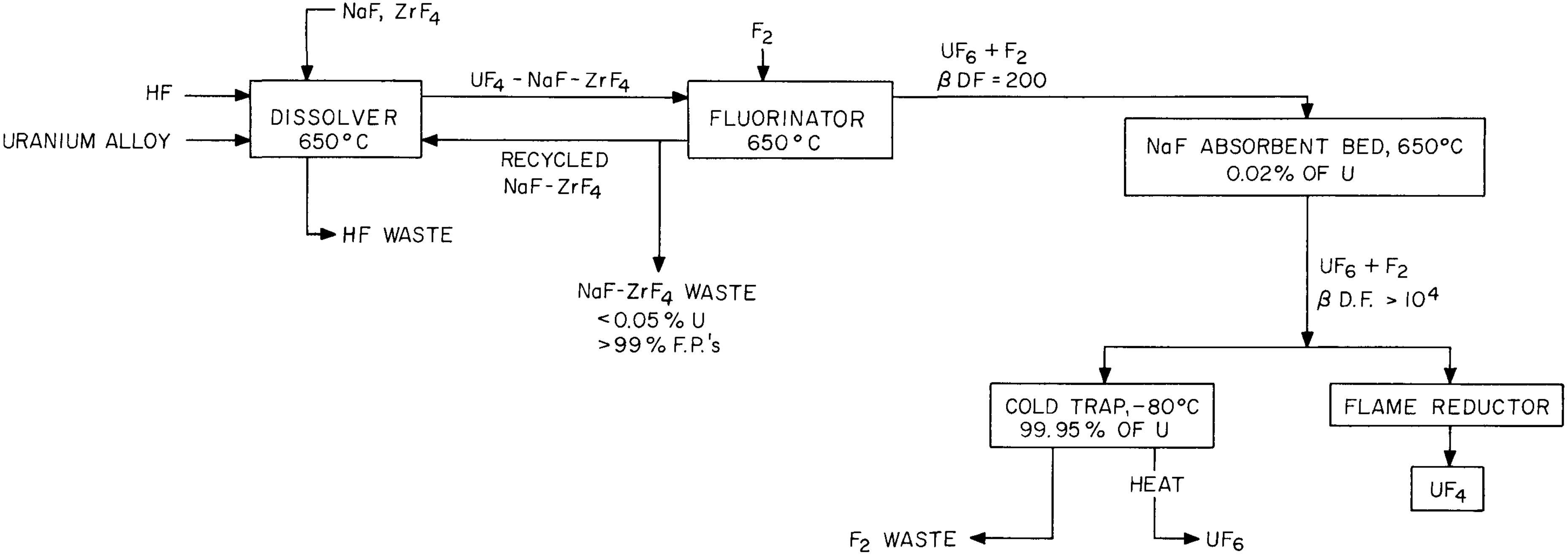

Fig. 1 Schematic Chemical Flowsheet for Fused Salt-Fluoride Volatility Process for Recovering Uranium from Heterogeneous Reactor Fuel. The flame reductor is described in reference 1.

A variation of the NaF absorption bed technic might be useful in obtaining good decontamination of short-decayed fuel. This would consist in using the bed at 100-300°C to absorb the UF_6 product, while such fission product fluorides as IF_7, MoF_6, and TeF_6 would pass through with the excess fluorine. The UF_6 would then be driven off by raising the bed temperature to 650°C in the presence of fresh fluorine.

2.0 INTRODUCTION

A fused salt—fluoride volatility process for recovering uranium from irradiated heterogeneous reactor fuel elements offers the advantages of compactness of equipment, disposal of most of the radioactive fission product waste as a solid, and operation at atmospheric pressure. In preliminary studies(2) zirconium-uranium alloys dissolved in fused $NaF-ZrF_4$ with HF at the reasonable rate of 20-50 mils/hr. Fluorination studies(3) indicated that the UF_6 evolved from the fluorinator would be decontaminated by a factor of 100-300. The present report describes experiments on further decontamination of the volatilized UF_6 by methods other than high-pressure distillation and gives data on the reaction kinetics and corrosion encountered in the fluorination step.

3.0 EXPERIMENTAL PROCEDURES

All fluorinations were carried out in reactors of type A nickel, which consisted of a 6-in. length of 1-in.-dia tubing fitted with a piece of 1/2-in.-dia tubing for the outlet and 1/4-in.-dia tubing for the fluorine inlet and thermocouple well (see Fig. 2). A sieve plate made of 1/32-in. nickel stock was placed 1 in. from the bottom to give better dispersion of the gas passing up through the salt. The salt charge was usually about 70 g, giving a 2-in. depth of salt in the reactor.

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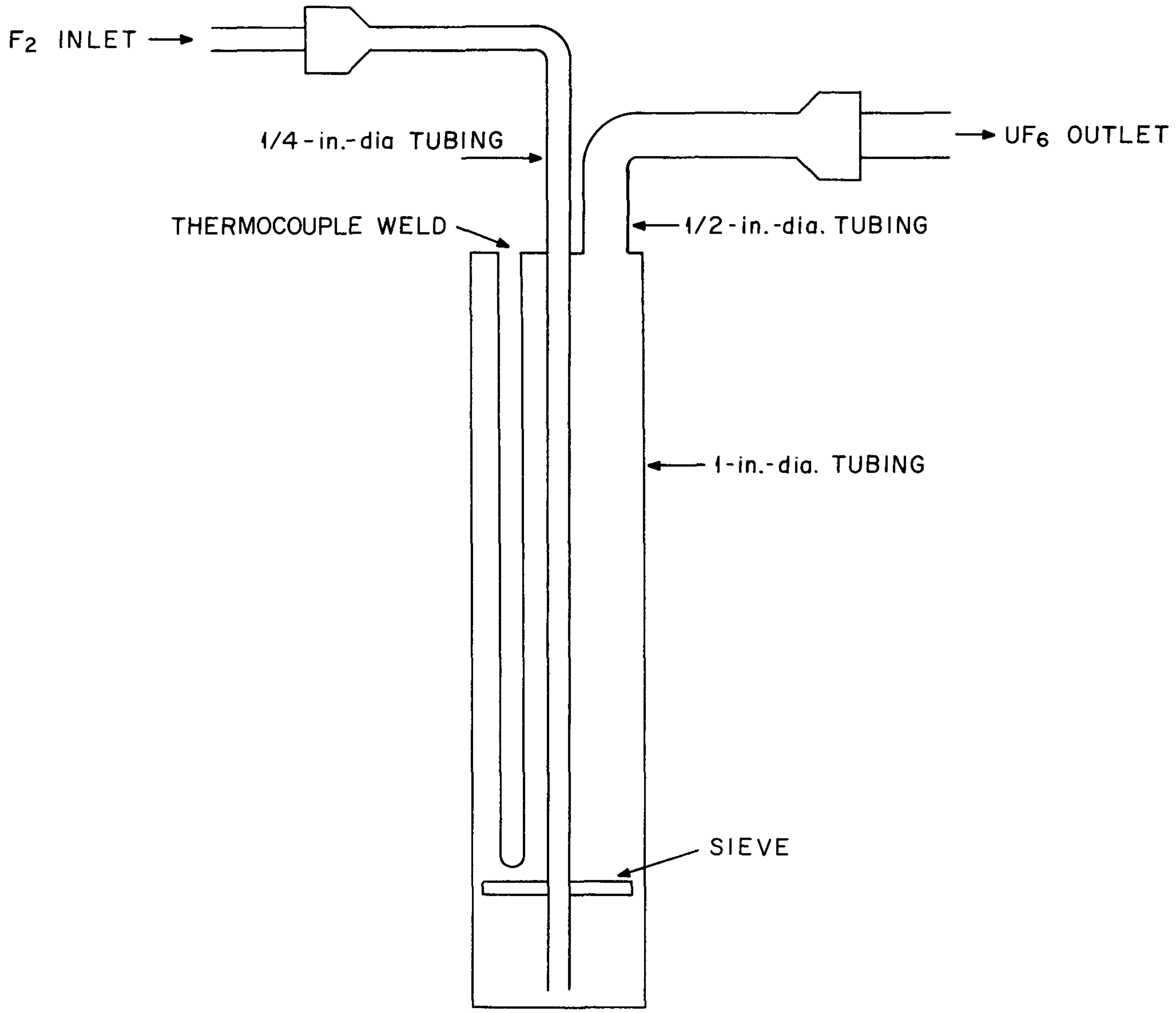

Fig. 2. Diagrammatic Sketch of Nickel Reactor.

The UF_6 was trapped in stainless steel vessels submerged in acetone—dry ice. The product UF_6 was hydrolyzed in the vessels with 1 $\underline{M}$ HNO_3-0.67 $\underline{M}$ $Al(NO_3)_3$ prior to being analyzed for total uranium and radioactivity. Copper tubing (1/4 in. dia) with flare fittings and brass Hoke valves were used in connecting the fluorination reactor to the trap and other parts of the assembly. In the decontamination studies the effluent $UF_6 + F_2$ was passed directly into the decontaminant being studied rather than immediately into the cold trap.

Fluorination experiments without activity present were made with a 4-52-44 mole % UF_4-NaF-ZrF_4 mixture. For runs with activity present, the salt was prepared by dissolving about 6 g of irradiated uranium metal in 67 g of NaF-ZrF_4 salt (55.5-44.5 mole %). The resultant UF_4-NaF-ZrF_4 salt had a composition of about 3.5-54.0-42.5 mole %.

Uranium metal was dissolved by passing HF, usually at a flow rate of less than 100 ml/min, through the molten NaF-ZrF_4 salt at 650°C for 12 hr. The penetration rate for uranium at this temperature is about 20 mils/hr.(2) The 12-hr period thus provided 2.4-fold the time estimated to be required for dissolution of the 200-mil-diameter miniature uranium slugs used.

Two batches of irradiated uranium metal were used. One had been irradiated to about 40 Mwd/ton and had decayed 30 days. The second batch, after an irradiation of 60 Mwd/ton, was permitted to decay 140 days to remove I^{131}.

Gas flow rates were measured with thermal flowmeters patterned after a design previously reported(4) (see appendix).

4.0 DECONTAMINATION STUDIES

Materials investigated for removing fission products from the UF_6-F_2 gas effluent from the fluorinator were a molten fluoride salt, a fluorocarbon liquid, and finely divided solid NaF. The decontamination factors of 50-100 obtained with NaF were 2-10 times greater than those obtained with the other reagents.

4.1 Decontamination by Scrubbing with NaF

An increase of 50-100 in the over-all ruthenium β decontamination factor was obtained by passing the fluorinator product through a bed of finely divided NaF (Table 1). In an exploratory trial (run 1), the UF_6-F_2 stream from the fluorinator was passed through a 30-g bed of 1/8-in. NaF pellets at 300°C. About 32% of the uranium was not absorbed by the NaF, while 38% had to be refluorinated from the NaF bed at 650°C before recovery as UF_6. However, the decontamination factors in the two fractions were of the same order, i.e., 2×10^3. The uranium loss on the NaF was only 0.01%. Two experiments were then performed with 30-g beds of 20- to 40-mesh NaF held at 650°C to eliminate the refluorination step (runs 2 and 3). In both tests the results showed high absorption of ruthenium and niobium, with over-all gross β decontamination factors of $>10^4$. The slight increase (less than 10) in decontamination from zirconium and total rare earths was probably due to de-entrainment rather than to absorption. The uranium loss on the NaF was 0.03% in run 3 where the NaF was carefully conditioned with fluorine at 650°C before use. In run 2, where there was no conditioning, the loss was 0.38%.

4.2 Decontamination by Scrubbing with Fused Salt

Three experiments on scrubbing volatilized UF_6 with 67 g of molten NaF-ZrF_4 (55.5-44.5 mole %) were carried out at 650°C (Table 2). The results indicated that scrubbing with fused salt is not so effective as with solid NaF in further decontaminating the UF_6, although it is perhaps a good de-entrainment procedure.

In run 4, an acetone—dry ice cold trap, in which the UF_6 was condensed and from which it was resublimed, was used between the

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Table 1

Decontamination of UF_6 by Solid NaF

UF_4-NaF-ZrF_4, 4-52-44 mole %, with a β activity of 1.2×10^6 c/m/mg uranium, fluorinated at 650°C

Run 1: UF_6 product plus 28-fold excess fluorine passed through 30-g bed of NaF pellets (1/8 in.) held at 300°C; 38% (fraction A) was absorbed and then refluorinated off at 650°C into an acetone—dry ice trap, while 32% (fraction B) was not absorbed and was directly trapped

Run 2: UF_6 product plus 11-fold excess fluorine passed through 30 g of 20- to 40-mesh NaF held at 650°C, and then trapped

Run 3: UF_6 product plus 9-fold excess fluorine passed through 30 g of 20- to 40-mesh NaF held at 650°C, and then trapped

	β Decontamination Factors						
	Run 1			Run 2		Run 3	
Activity	Fraction A	Fraction B	Scrub[(a)]	Over-all	Scrub[(a)]	Over-all	Scrub[(a)]
Gross β	2200	1600	3.5	2.3×10^4	50	1.6×10^4	24
Ru β	140	120	3.0	5200	90	3100	50
Zr β	4300	870	1.6	4.1×10^4	7.3	8.3×10^4	9.4
Nb β	430	47	17	3400	280	2500	100
TRE β	10^6	5×10^4	3.5	3×10^5	7.3	4×10^6	2
Uranium Losses (% of initial charge)							
In fluorination salt	0.04			0.02		0.01	
In NaF bed	0.01			0.38		0.03	

(a) Calculated for absorption step alone on basis of activity found in NaF.

Table 2

Decontamination of UF_6 by Molten NaF-ZrF_4

Runs 4 and 5, UF_4-NaF-ZrF_4, 4-52-44 mole %, with a β activity of 3.7 x 10^6 c/m/mg uranium

Run 6, UF_4-NaF-ZrF_4, 4-52-44 mole %, with a β activity of 1.2 x 10^6 c/m/mg uranium

Run 4: fluorination period of 5 hr; UF_6 condensed in cold trap and resublimed from it prior to scrubbing; UF_6 recovered from scrub by refluorination

Run 5: fluorination period of 3 hr; UF_6 plus excess fluorine passed directly to scrub salt from fluorination step and trapped

Run 6: fluorination period of 4 hr; UF_6 plus excess fluorine passed directly to scrub salt from fluorination step, trapped and resublimed

Scrub salt: NaF-ZrF_4, 55.5-44.5 mole % at 650°C

	β Decontamination Factors					
	Run 4		Run 5		Run 6	
Activity	Scrub[(a)]	Over-all	Scrub[(a)]	Over-all	Scrub[(a)]	Over-all
Gross β	---	2 x 10^{4}[(b)]	---	2 x 10^{4}[(b)]	2.7	4800
Ru β	1.4	430	6	750	2.3	350
Zr β	9	1 x 10^5	3	>7 x 10^4	---	3.2 x 10^4
Nb β	8	2 x 10^4	4	700	47	1800
TRE β	3	2 x 10^6	90	>8 x 10^6	---	2 x 10^6
Cs β	---	---	130	>3 x 10^4		
Sr β	---	---	20	>3 x 10^6		
Ba β	---	---	---	>8 x 10^5		

Uranium Losses (% of initial charge)

	Run 4	Run 5	Run 6
In fluorination salt	0.03	1.6	0.01
In scrub salt	0.01	0.23	0.02

(a) Calculated for scrub step alone on basis of activity found in scrub material.

(b) Calculated on the gross Ru, Zr, Nb, and total rare earth activity rather than total activity, which included much due to I^{131}.

fluorination and scrub steps. The uranium was recovered from the scrub salt by refluorination. In runs 5 and 6 the UF_6 was not trapped and sublimed prior to scrubbing. Run 6 differed from run 5 in the addition of a tail-end sublimation step.

The scrub decontamination factors (see Table 2) were calculated on the basis of the activity remaining in the scrub salt. The gross β decontamination factor of 20,000 obtained in runs 4 and 5, in which the material fluorinated corresponded to short-decayed uranium, is about fivefold greater than the 4000-5000 values obtained previously(3) in fluorination tests followed by sublimation of the UF_6 product. The decontamination factors for individual fission products are somewhat uncertain because of the high amount of short-decayed material, particularly 8-day I^{131}, in the product. The gross β decontamination factor of 4800 in run 6, in which long-decayed material was processed, is very close to that reported previously(3) for fluorination plus resublimation of the product.

The decontamination obtained in fused salt scrubbing was best evaluated by determining the amount of radioactivity actually remaining in the scrub salt. On this basis the increase in ruthenium and niobium β decontamination due to the scrub step was less than 10. Results in run 5 indicated that some rare earth, cesium, and strontium β activity decontamination occurred in the scrub salt, possibly as a result of de-entrainment of these nonvolatile fluorides. A fused salt scrub would perhaps be valuable for this purpose in processing very highly burned up (1-30%) fuel.

4.3 Decontamination by Scrubbing with a Fluorocarbon, C_8F_{16}

No significant decontamination was obtained by scrubbing the UF_6 product from the fluorination and sublimation steps with a fluorocarbon, C_8F_{16} (Table 3). Approximately 9 g of UF_6, sublimed from a trap used to collect the product of a fluorination run, was passed very slowly into the bottom of a C_8F_{16} distillation column (0.5 in. dia, 14 in. high,

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packed with 3/32-in. nickel Fenske helices) that was operating at full reflux at about 102°C. The UF_6 was taken out of the still as gas through an 80°C partial stillhead. The over-all ruthenium β decontamination factors of 14 and 16, respectively, obtained in two runs were about the same as those obtained in the fluorination step alone.(3) The ruthenium behavior indicated the possible presence of RuF_8 rather than of RuF_5 since the latter is a high-boiler in comparison to C_8F_{16} or UF_6.

Table 3

Decontamination of UF_6 by C_8F_{16}

UF_6 produced by fluorination of UF_4-NaF-ZrF_4, 4-52-44 mole %, with a β activity of 1.2×10^6 c/m/mg uranium; UF_6 product separated from excess fluorine in an acetone—dry ice trap and then volatilized through a C_8F_{16} still into a second trap

	β Decontamination Factors			
	Run 7		Run 8	
Activity	Over-all	Scrub(a)	Over-all	Scrub(a)
Gross β	290	1.2	250	2.2
Ru β	16	---	14	---
Zr β	6.8×10^4	---	4.7×10^4	---
Nb β	1200	---	86	---
TRE β	2×10^6	---	2×10^5	---

(a) Calculated for scrub step alone on basis of activity found in scrub material.

4.4 Material Balance of Activities

Poor material balances for ruthenium and niobium were observed in all fluorination runs. Generally, 1 to 10% of the initial ruthenium content and about 50% of the initial niobium content remained in the fused salt waste. After one run (run 3; see Table 1), the nickel fluorination vessel was cut into three parts and dissolved in dilute nitric acid, and the niobium and ruthenium in each portion of the vessel were determined (see Table 4). Nearly all the niobium activity was accounted for in the reactor and fused salt, while 75% of the ruthenium was apparently volatilized out of the reactor entirely. The remaining ruthenium plated out heavily on the metal walls of the reactor. The distribution ratio between the metal wall and the fused salt was about 5 for ruthenium and less than 0.01 for niobium.

Table 4

Material Balance for Ruthenium and Niobium Activity in Fluoride-Volatility Run 8

Location	Activity (% of original)	
	Ru β	Nb β
Bottom of reactor (in contact with fused salt)	4	0.4
Top of reactor (not in contact with fused salt)	8	3
Outlet tube	10	27
Fused salt waste	0.8	69
NaF absorbent	2	1
Total	25	100

The material balance for total rare earths, zirconium, strontium, barium, and cesium activity was always about 100% since the fluorides of these elements are relatively nonvolatile.

The behavior of plutonium in the fluorination step is important in processing fuel that has a high proportion of U^{238}. Results of many fluorination runs at 650°C have shown that only about 0.01% of the plutonium is carried over with the UF_6 product. The uranium decontamination factor with respect to plutonium was therefore about 10^4.

5.0 KINETICS OF FLUORINATION REACTION

Two methods were used in studying the kinetics of the fluorination reaction. The first consisted in passing the exit gas from the fluorination vessel first through a trap filled with NaF (1/8-in. pellets) and then through a trap filled with NaCl (coarse powder). The NaF trap, held at about 100°C, trapped UF_6 by absorption. The NaCl trap, also at 100°C, lost weight as the NaCl was converted to NaF by the fluorine. Weighing such traps at intervals provided a means of following the progress of the fluorination. Wet potassium iodide paper furnished a very rapid visual test for fluorine. The second method (see Fig. 3) consisted in using three thermal flowmeters (see appendix) to measure the fluorine input flow rate, the combined UF_6 and fluorine output flow rate, and the fluorine output flow rate after any UF_6 in the gas stream had been absorbed in NaF. A Brown 5-mv recorder was used to obtain flow readings at 20-sec intervals. The NaF and NaCl absorption trap technic provided a method of calibrating the flowmeters for F_2 and UF_6. Study of the kinetic behavior was more precise in the flowmeter method than in the absorption trap method owing to the semicontinuous recording.

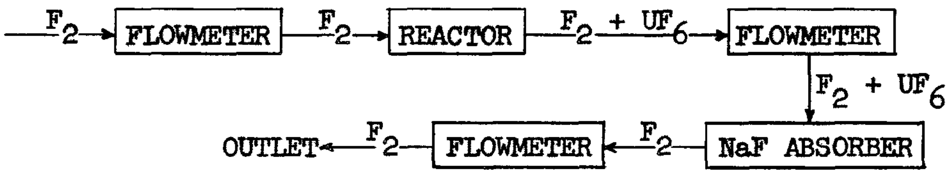

Fig. 3. Schematic Diagram of Flowmeter Method of Measuring Gas Flow Rates in Fused Salt—Fluoride Volatility Process.

Results with the absorption trap procedure showed nearly 100% fluorine utilization in volatilizing about 80% of the uranium as UF_6. This behavior was confirmed when the reaction was followed by the flowmeter method.

The variation in flow rate with time in one fluorination run in which three thermal flowmeters were used is shown in Fig. 4a. Three curves were obtained. The first curve shows the fluorine input rate, which remained practically constant throughout the run. The second curve gives the flow of gas from the reactor to the NaF trap; a UF_6 calibration curve was used to interpret this flow. However, the first part of this curve is somewhat in error since the system originally contained nitrogen, and nitrogen or a mixture of nitrogen and UF_6 initially passed through the second flowmeter. The third curve gives the output flow from the NaF trap. The gas passing through this meter was initially nitrogen; it was fluorine after 31 min, at which time nitrogen displacement was complete and a chemical test for fluorine was first obtained. The hump in the nitrogen part of the third flowmeter curve results from displacement of nitrogen gas by UF_6 from the apparatus between the reactor and flowmeter. The initial flow of about 5 ml/min may have been due to some inert impurity in the fluorine supply.

The flowmeter readings are interpreted in Fig. 4b to show the UF_6 and fluorine evolution as a function of time. During the first 14 min fluorine was nearly completely absorbed. Material balance calculations indicated that only about half this amount of fluorine could be attributed to the reaction $UF_4 + F_2 \longrightarrow UF_6$. The remainder is assumed to have been utilized in corrosion. At the end of 14 min, UF_6 evolution began and after about 20 min increased to 35-40 ml/min. The UF_6 evolution remained essentially constant over the next 10 min and began to drop off simultaneously with the breakthrough of fluorine, which occurred after 30 min.

The fluorine absorption was essentially complete until 85% of the UF_6 had been evolved. Based on the amount of fluorine absorbed during this period, an average corrosion rate of 4 mils/hr was calculated.

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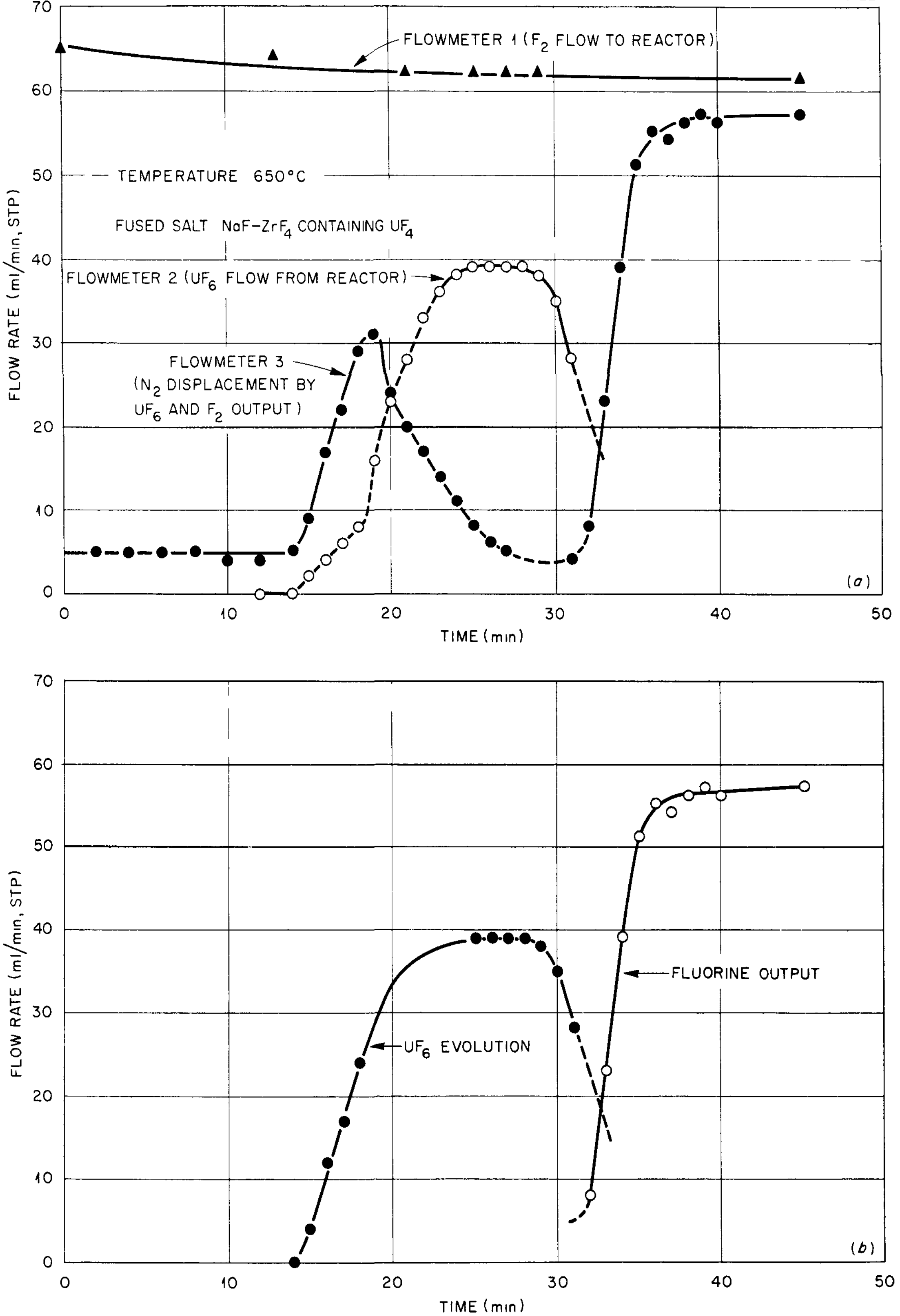

Fig. 4. (a) Gas-Flow Characteristics in Fused Salt Volatility Process; (b) Kinetics of Fluorination Step. Dotted lines indicate uncertainty resulting from mixing of gas with nitrogen.

Qualitative work (Sec. 6.0) on the solubility of UF_6 in a $NaF-ZrF_4$ mixture suggested the existence of a stable $NaF-UF_6$ complex that is soluble in molten $NaF-ZrF_4$. The induction period and the subsequent plateau in UF_6 production shown in Fig. 4a and b are also indicative of this. The reaction mechanism is believed to be:

$$UF_4 \text{ (solution in } NaF-ZrF_4) + F_2 \text{ (gas)} \longrightarrow xNaF \cdot UF_6 \text{ (solution in } NaF-ZrF_4) \longrightarrow UF_6 \text{ (gas)}$$

The induction period is the result both of fluorine consumption in corrosion and of a buildup in the concentration of the $NaF-UF_6$ complex until the saturation solubility is reached. Then UF_6 begins to evolve as fast as fluorine is supplied in excess of the rate of utilization in corrosion. The possibility that oxides dissolved in the fused salt could account for the delay in UF_6 generation was discounted by the results of a run in which fluoride fuel was sparged with HF for 45 min and then with nitrogen for 10 min. Any oxides present would have been eliminated by this treatment, but the induction period was the same as that in the run plotted in Fig. 4a and b.

The Na/Zr atom ratio in the fluoride salt studied was about 5/4. Addition of more ZrF_4 to this fuel to change this ratio to 4/5 had practically no effect on the curves shown in Fig. 4a and b. This suggests that the $NaF-ZrF_4$ complex is relatively weak in comparison to the interaction between NaF and UF_6. The main effect of a change in the Na/Zr ratio is on the melting point of the salt mixture.

6.0 CHEMICAL INTERACTION OF UF_6 WITH NaF

Additional evidence on the interaction of UF_6 with molten $NaF-ZrF_4$ and solid NaF at high temperatures was obtained in various tests. Martin, Albers, and Dust(5) reported that UF_6 and NaF forms a complex at moderate temperatures according to the reaction

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$$UF_6 \text{ (gas)} + NaF \text{ (solid)} \longrightarrow 3\ NaF \cdot UF_6 \text{ (solid)}$$

which then breaks down above 450°C to free fluorine and the quadrivalent state of uranium by the reaction

$$3NaF \cdot UF_6 \text{ (solid)} \longrightarrow NaF \cdot UF_4 \text{ (solid)} + 2NaF \text{ (solid)} + F_2 \text{ (gas)}$$

These conclusions appear to be valid according to the exploratory tests conducted in conjunction with the decontamination and kinetic studies. Moreover, there is considerable evidence which indicates that the same processes occur in the liquid state at high temperatures with molten NaF-ZrF_4.

A summary of the conclusions drawn from these experiments will be given rather than a detailed description since the work was very rough. The results with respect to molten NaF-ZrF_4 are fairly complete and agree very well with the conclusions drawn from the kinetic data. The work on solid NaF is more incomplete, but nevertheless indicates some of the complexity present in use of a NaF bed for securing UF_6 decontamination.

It was concluded that UF_6 is soluble in molten NaF-ZrF_4 (55.5-44.5 mole %) at 500-700°C to the extent of 38 g of UF_6 per 100 g of salt. Pure UF_6 can be completely absorbed in molten NaF-ZrF_4 owing to the high solubility when no accompanying gas is present. If the UF_6 is mixed with another gas, e.g., helium, part of the UF_6 is not absorbed.

Free fluorine is evolved slowly from a solution of UF_6 in molten NaF-ZrF_4. This is detectable by passing helium over the salt and testing the helium with wet potassium iodide paper (no starch). A negative potassium iodide test was obtained with the UF_6 used in this series of experiments.

A solution of UF_6 in molten NaF-ZrF_4 corrodes a nickel reactor at the very high rate of about 1 mil/hr. This rate was calculated from the reactor surface area and the nickel content of the salt as determined by analysis. In one experiment the amount of nickel corrosion was equivalent to the reduction of 33% of the UF_6 to UF_4. The equation for the reaction is

$$NaF \cdot UF_6 \text{ (solution)} + Ni \text{ (solid)} \longrightarrow NiF_2 \text{ (solution)} + NaF \cdot UF_4 \text{ (solution)}$$

UF_6 gas can be absorbed by solid NaF (20-40 mesh) at 100°C to the extent of 100 g per 100 g of salt. When the UF_6-NaF solid complex is heated, part of the UF_6 is evolved along with free fluorine at temperatures in the range 340-600°C. In one experiment with an initial loading of 100 g of UF_6 per 100 g of NaF, 63% of the uranium remained in the NaF after the solid complex had been heated to 600°C where most of the gas evolution ceased. This can be accounted for by the second equation of Martin et al.

Passage of UF_6 through a NaF bed at 650°C gives a salt with a uranium content of only 2%. Most of the UF_6 appears to pass through the reactor without decomposition except at the reactor wall. Only a very slight indication of free fluorine can be obtained.

7.0 CORROSION STUDIES

The corrosion work to date has consisted mainly of gravimetric tests on metal coupons and determinations of nickel in the fused salt residues from fluorination studies (see Table 5). In the gravimetric tests the corrosion rate was generally less than 0.1 mil/hr for nickel, and somewhat higher for Inconel and Monel.

The average corrosion rate was higher in the runs in which UF_4 was present than in the others. In these five runs there was a UF_4-to-UF_6 conversion period of less than 1 hr, followed by a period of several hours during which fluorine was passed through the salt. The average corrosion rate was, in general, greater in the short runs, which is believed to be because of the very high corrosion during the time that UF_6 was present. The lower average corrosion rate in long runs is due to less corrosion occurring after the uranium had all been evolved.

The corrosion rates determined from salt analyses were obtained in five fluorination runs made with NaF-ZrF_4-UF_4. The test periods were probably greater than specified since the time spent in starting or

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Table 5

Corrosion in Fused Salt—Fluoride Volatility Process at 650°C

Gravimetric studies: corrosion coupons cut from round rod weighed and immersed in fused salt, through which fluorine was being passed, for time shown, and reweighed

Salt analyses studies: fused salt residue from fluorination studies carried out in nickel reactors were analyzed for nickel

Salt(a)	Test Period (hr)	Corrosion Rate (mils/hr)		
		Ni	Inconel	Monel
	Gravimetric Method			
$NaF-ZrF_4$ (56-44 mole %)	14(b)	0.031	0.021	0.016
	14(b)	0.36	0.40	0.76
$NaF-ZrF_4-UF_4$ (52-44-4 mole %)	8(c)	0.056	0.063	0.12
	5.5(c)	0.081	0.017	0.11
	6.5(c)	0.066	0.11	0.15
	8(c)	0.077	0.064	0.48
	1(c)	0.37	0.56	0.44
$NaF-ZrF_4$ (56-44 mole %)	1(c)	0.058	0.10	0.10
	Salt Analyses			
$NaF-ZrF_4-UF_4$ (52-44-4 mole %)	1.5	0.66		
	3	0.33		
	4	0.06		
	5	0.25		
	5	0.21		

(a) Two runs were made with the first batch of salt. In all other experiments a fresh batch of salt was used in each run.

(b) Same corrosion samples used in the two successive runs.

(c) Same corrosion samples used in the six successive runs.

stopping each experiment is not accurately known. The internal surface area of the nickel reactor used in each run was about 66 sq cm. The highest corrosion rate, 0.66 mil/hr, was again obtained in the run of shortest duration.

Some information on corrosion can also be obtained from the kinetic data in Fig. 4a and b. The discrepancy between the maximum UF_6 flow rate of 40 ml/min and the fluorine flow rate of 62 ml/min represents a nickel corrosion rate of about 1.8 mils/hr. This corrosion rate is perhaps effective only during the period of existence of the NaF-UF_6 complex. However, an even more rapid average corrosion rate of 4 mils/hr during the time that UF_6 was present was indicated by the fluorine material balance. The low values for corrosion rates obtained in the gravimetric test and fused salt analyses are possibly obtained only over the process as a whole, i.e., when the UF_4-to-UF_6 conversion period is accompanied by several hours of fluorine sparging to remove the last traces of uranium.

In some laboratory fluorination runs, 50% or more of the fluorine was consumed in corrosion of the nickel reactor. This need not be true in scaling up the process to a pilot plant level. It is estimated that the consumption of fluorine in corrosion for a 10-kg uranium batch will be less than one-tenth that in a batch of 6 g. This is a consequence of the greater volume-to-surface ratio in the 10-kg case.

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Appendix

9.0 USE OF THERMAL FLOWMETER WITH CORROSIVE GASES

The thermal flowmeter described by Johnsson, Peed, and Clewett(4) has been found very useful for measurement of small flows of corrosive gases such as F_2, UF_6, and HF, as well as for the inert blanket gases, nitrogen and helium. Figure 5 is a sketch of one type of thermal flowmeter design used in the fused salt—fluoride volatility process development work. The original design was modified by increasing the size of the heat reservoir in the brass base. The reservoir in the modified design consists of a 4-in. length of 2.5-in.-dia bar stock. Better equilibrium of the entrant gas temperature was thereby obtained. In a further modification of this design the gas entered the instrument through 1/4-in.-dia copper tubing wound around the base, to secure better temperature equilibrium. The heavy 1/8-in.-dia wall of the cover provides a very stable ambient temperature around the legs of the U tube. The instrument is designed for a useful range of 20-500 ml/min with 10 watts applied to the heater. The response is sufficiently rapid for obtaining 20-sec-interval readings on a 5-mv Brown recorder.

Each instrument was individually calibrated for different gases. A temperature of 80°C for the thermal flowmeter was employed with HF and UF_6. This was achieved by placing it on a laboratory hot plate controlled by a Variac. In the case of nitrogen, helium, or fluorine, room temperature operation was satisfactory. A wet test meter was used for calibrating the instrument for use with noncorrosive gases. Calibrations for HF were obtained by trapping and weighing the HF after it had passed through the flowmeter. UF_6 calibrations were obtained by trapping the UF_6 on NaF held in a nickel tube at 100°C. The calibrations for F_2 were made by passing the F_2 into a NaCl tube and measuring the weight loss due to conversion to NaF.

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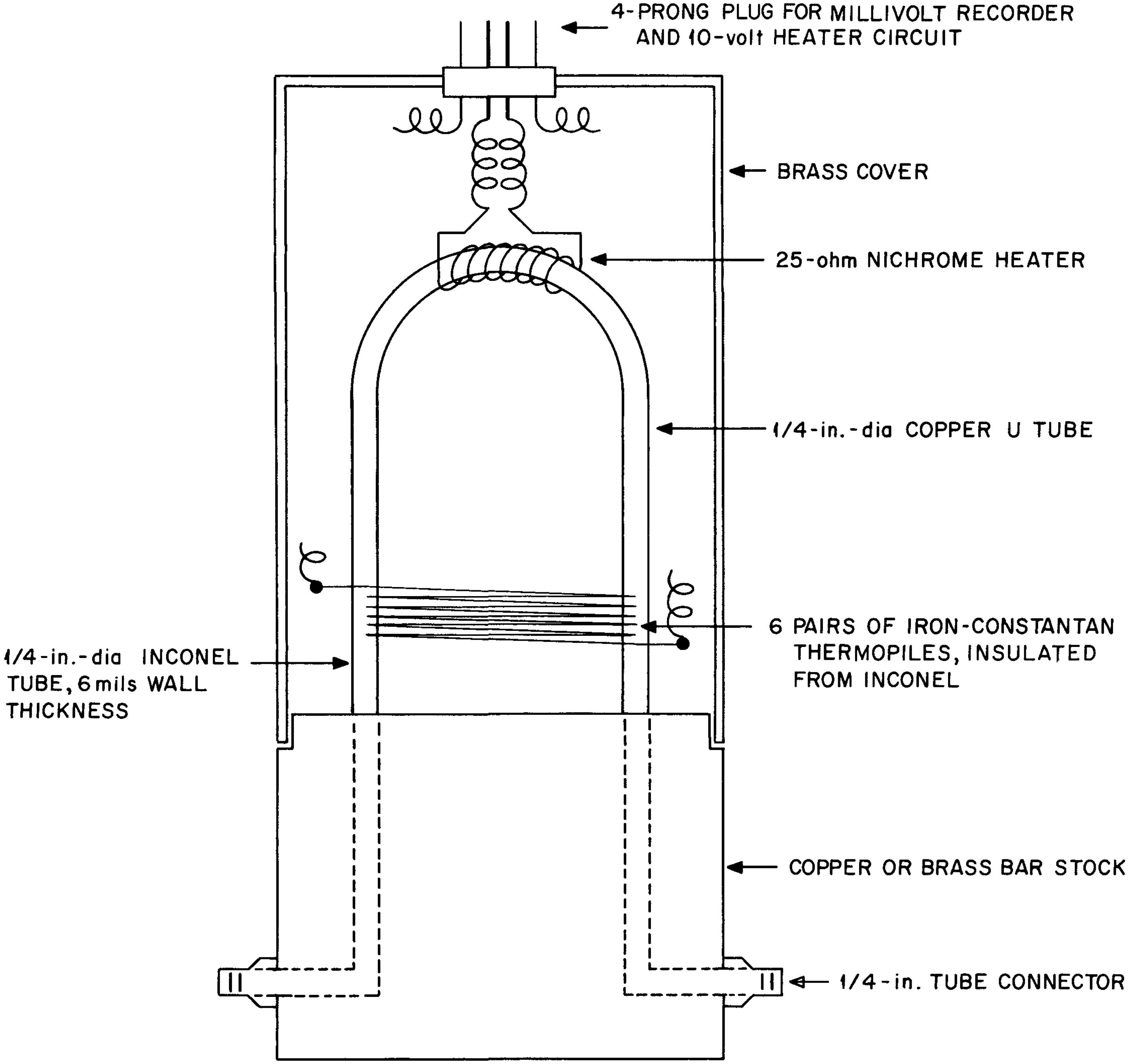

Fig. 5. Thermal Flowmeter.

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