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Special Features of Aircraft Reactors

EFFECT OF RADIATION ON CORROSION OF STRUCTURAL MATERIALS BY MOLTEN FLUORIDES

G. W. Keilholtz
J. G. Morgan
W. E. Browning

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Abstract

A survey of the experimental methods used in testing the radiation stability of molten salts and their corrosion properties is presented. The effects of irradiation on the corrosion on Inconel exposed to fluoride fuel mixtures and on the physical and chemical stability of the fuel mixtures have been investigated by irradiating in the MTR capsules filled with static fuel and by operating in-pile forced-circulation loops in the LITR and in the MTR. In the many capsule tests and in the three in-pile loop tests made to date, no major changes have occurred in the fuel mixtures that can be attributed to irradiation, other than normal burn-up of uranium. Metallurgical examinations of the Inconel capsules and tubing have likewise shown no changes in corrosion that can be the result of radiation damage. The low corrosion results obtained for the in-pile loops have been confirmed by chemical analyses for corrosion products in the fuel mixtures.

The use of molten fluorides as reactor fuels (1) requires that they be stable both thermally and in intense radiation fields. The fission process in the salt causes regions of high ionization density to exist, as well as very high heat fluxes. However, since molten salts are generally ionic liquids, there is no crystalline lattice to disrupt, nor are there covalent bonds to sever. Thus, fast neutrons, fission fragments, and gamma radiation cannot cause severe damage of the type found in crystalline materials. However, the interface between the molten salt and its container offers a site where radiation effects might make themselves evident in an acceleration of the corrosion process. With this possibility, it has been necessary to test the compatibility of various salts with structural metals in the highest neutron fluxes available.

The principal methods used in in-pile testing of molten salts are listed in Table I. Capsule tests were performed first because of their simplicity and their ability to produce information susceptible to statistical analysis. The successive techniques listed in the table are of increasing degrees of complexity and approach closer and closer to the design conditions of a practical nuclear power plant. Each step, however, introduces new variables and requires far greater expenditure of effort and time than the previous step does, rapidly decreasing the number of tests which can be performed. Although consideration was given to their use, rocking capsule tests and thermal convection loops have not formed a part of the work described here.

Capsule tests have been made with nickel, types 316 and 347 stainless steel, and Inconel. The salts employed and their compositions are listed in Table II. The first salt irradiations were conducted by Van De Graaf (2) and cyclotron (3) bombardments. Proton bombardments (3b)were employed to

TABLE I

METHODS OF STUDYING RADIATION EFFECTS ON CORROSION BY MOLTEN FLUORIDE FUELS

1. In-Pile Capsule Tests
2. Rocking Capsule Tests
3. Thermal Convection Loops
4. Forced-Flow Loops
5. Experimental Reactors

TABLE II

MOLTEN SALTS TESTED IN RADIATION EFFECTS PROGRAM

System	Composition (mole%)
KOH	100
$NaF-KF-UF_4$	46.5-26.0-27.5
$NaF-BeF_2-UF_4$	25.0-60.0-15.0
$NaF-BeF_2-UF_4$	47.0-51.0-2.0
$NaF-BeF_4-UF_4$	50.0-46.0-4.0
$NaF-ZrF_4-UF_4$	63.0-25.0-12.0
$NaF-ZrF_4-UF_4$	53.5-40.0-12.0
$NaF-ZrF_4-UF_4$	50.0-48.0-2.0
$NaF-ZrF_4-UF_3$	50.0-48.0-2.0

supplement parallel experiments in the ORNL Graphite Reactor because of the high specific power attainable in this way. These irradiations were continued for 1 to 92 hours, using 20 to 22 Mev. protons in the ORNL 86-in. cyclotron. Specific power generation ranged from 500 to 4700 watts cm^{-3}. With the starting of the MTR, a sufficiently high-flux reactor became available for these experiments. Irradiation with neutrons, gamma rays, and fission fragments obtained in this way are far more realistic than those using elementary charged particles. The emphasis was therefore shifted to reactor irradiations.

A typical capsule used in the MTR irradiation program is shown in Fig. 1. It is 0.100 in. i.d. with a 0.050 in. wall. The length of the salt column is 1 in. In salts with high U^{235} contents, the diameter of the fuel column is reduced to 0.055 in. This avoids excessive temperatures at the center of the salt colume when working with fuels generating as high as 8000 watts cm^{-3} (4). Fig. 2 illustrates the arrangement of control instrumentation on the north balcony of the MTR. Electrical and cooling-air lines extend from the instrument panels to the top of the reactor. The capsule is loaded through the reactor inlet water line. It is inserted down an aluminum tube into a beryllium piece located in the reflector region. Fig. 3 shows the MTR irradiation facility. The temperature of the fuel is controlled by a variable flow of air, the outer surface temperature of the capsule being monitored with thermocouples. The weight of salt is chosen so that about 250 watts of fission heat are generated in the capsule. This requires about 3 cfm of cooling air. Using 45 psig air, the velocity through the capsule restriction is about 700 $ft.sec.^{-1}$.

It was necessary to develop special thermocouple junctions for use in such high-velocity cooling air streams. The air produces a large thermal

gradient in the capsule wall and in the thermocouple beads. In poorly constructed thermocouples, errors as great as 300°C have been observed. The thermocouple shown in Fig. 4 was made by a resistance spot-welding technique. The bead is designed to have a large area of contact with the capsule and to be very thin, thus ensuring that the part which measures temperature is at the same temperature as the surface of the capsule.

After irradiation, capsules are returned to ORNL where detailed examinations are made in the Solid State Division hot cells. Fig. 5 shows a cell equipped for chemical analyses. Right-to-left are a vertical lathe for opening capsules, a master-slave manipulator, a drill press for removing salt samples, and a chemical hood. Operations involving radioactive powders are enclosed in lucite cases which are exhausted through a filter system. Fig. 6 shows a tool for slitting capsules longitudinally (5), to obtain specimens sometimes desired for metallographic studies. Fig. 7 shows the hot cell in which metallographic specimens are prepared (6). Some salt samples have been examined using the shielded petrographic microscope (7) shown in Fig. 8.

The principal variables studied in the static corrosion program have been flux, fission power, time, and temperature. In a fixed neutron flux, the fission power is varied by adjusting the U^{235} content of the fuel mixture. Thermal neutron fluxes have ranged from 10^{11} to 10^{14} neutrons cm^{-2} $sec.^{-1}$ and fission power-densities from 80 to 8000 watts cm^{-3}. Capsules have generally been irradiated for 300 hours at 1500°F (815°C), although in recent tests the experiments have been extended to 600 to 800 hours. The techniques used for examining capsules after irradiation are listed in Table III.

TABLE III

TECHNIQUES FOR EXAMINING IRRADIATED MOLTEN FLUORIDES

1. Pressure Tests (In-Pile)
2. Melting Point Determinations
3. Petrographic Analyses
4. Chemical Analyses
5. Mass Spectroscopic Assays
6. Gamma-Ray Spectroscopic Studies
7. Metallographic Examination of Containers

In the many capsule tests to date (over 100), no major changes have been observed which can be attributed to irradiation, except the normal burn-up of U^{235}. Metallographic examinations (8) of Inconel capsules tested in $NaF-ZrF_4-UF_4$ and in $NaF-ZrF_4-UF_3$ at 1500°F for 300 hours have shown corrosion comparable to that found in unirradiated control tests, i.e., penetrations to depths of less than 4 mils. In capsules which experienced accidental excursions to 2000°F and above, there was penetration to depths of more than 12 mils, accompanied by grain growth. These results stimulated extensive development work on control instrumentation and thermocouple construction. Chemical determinations of chromium in irradiated salts have been shown (9) to be seriously affected by the intense beta radiation of the accompanying fission products. Work is currently in progress on the circumvention of this problem.

Three typesof forced-circulation in-pile loops have been studied. A large loop was operated in a horizontal beam-hole of the LITR (10). The pump for circulating the fuel in this loop was placed outside the reactor shield. A smaller loop was operated in a vertical position in the lattice of the LITR (11), its pump mounted just above the lattice. A third loop was operated completely within a beam-hole of the MTR (12). The operating conditions for these loops are presented in Table IV. The dilution factor for a reactor may be defined as the ratio of the total volume of fuel in the system to that in the reactor core. A more useful definition for in-pile loop use is the ratio of the maximum specific power to the average specific power. In the two LITR loops, metallographic examinations showed less than 1 mil penetration of the Inconel fuel tubes. Figs. 9 and 10 show drawings of these two loop models. The MTR horizontal loop is shown in Fig. 11. Examination of etched and unetched metallographic sections of Inconel tubing from this loop showed no attack to a depth greater than 3 mils. A slight amount of intergranular corrosion was noted,

but this was neither dense nor deep. Measurements of wall thickness showed no variations attributable to corrosion. The loop was examined carefully for effects of temperature variations between inside and outside walls of the tubing at the bends, but no effects of overheating were observed. The low corrosion is attributable to careful temperature control of the salt-metal interface and to the maximum wall temperature being below 1500°F at all times. The larger corrosion value in the MTR loop results from the greater fuel-temperature differential (155°F) which was obtained during operation. Loops operated in the absence of radiation show similar effects. Studies of the behavior of fission product elements in these loops are discussed elsewhere (13).

The experiments described above show that, within the limits of tests to date, there is no acceleration by radiation of the corrosion of Inconel by molten fluoride reactor fuels. Experiments are planned to extend the program to cover new salt compositions and new alloys and to operate in-pile loops for much longer times with higher flow-rates and greater fuel-temperature differentials.

TABLE IV

OPERATING CONDITIONS FOR INCONEL FORCED-CIRCULATION IN-PILE LOOPS

	LITR Horizontal Loop	LITR Vertical Loop	MTR Horizontal Loop
Fuel Composition (mole%)	$NaF-ZrF_4-UF_4$ (62.5-12.5-25)	$NaF-ZrF_4-UF_4$ (63-25-12)	$NaF-ZrF_4-UF_4$ (53.5-40-6.5)
Max. Fission Power, watt cm^{-3}	400	500	800
Total Power	2.8	5.0	20
Dilution Factor	180	10	5
Max. Fuel Temp., °F.	1500	1500	1500
Fuel Temperature Differential, °F.	30	71	155
Fuel Reynolds' Number	6000	3000	5000
Operating Time, Hours	645	130	467
Time at Full Power	475	30	271
Depth of Corrosion Attack, mils	<1	<1	<3

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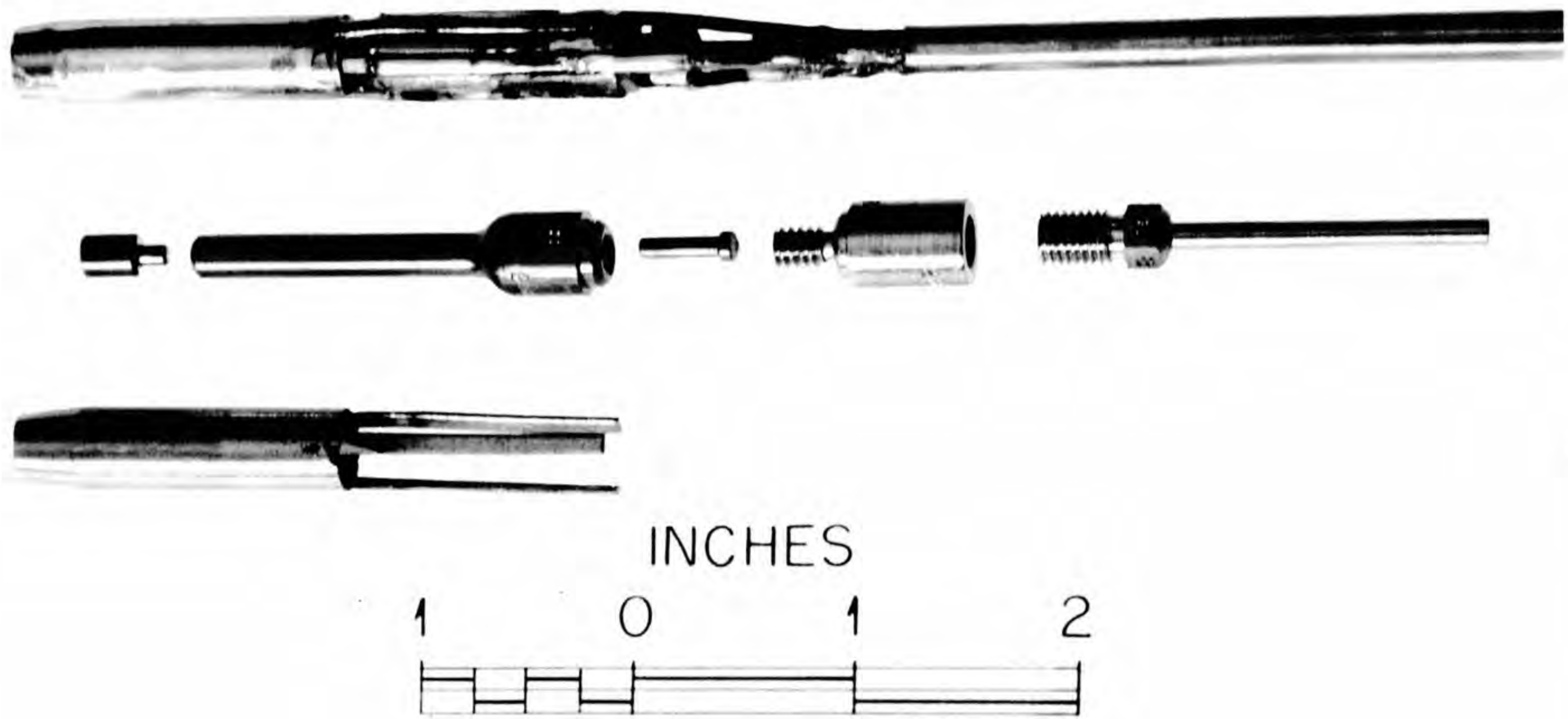

Fig. 1. A Typical Capsule for Irradiation of Molten Fluorides in the MTR.

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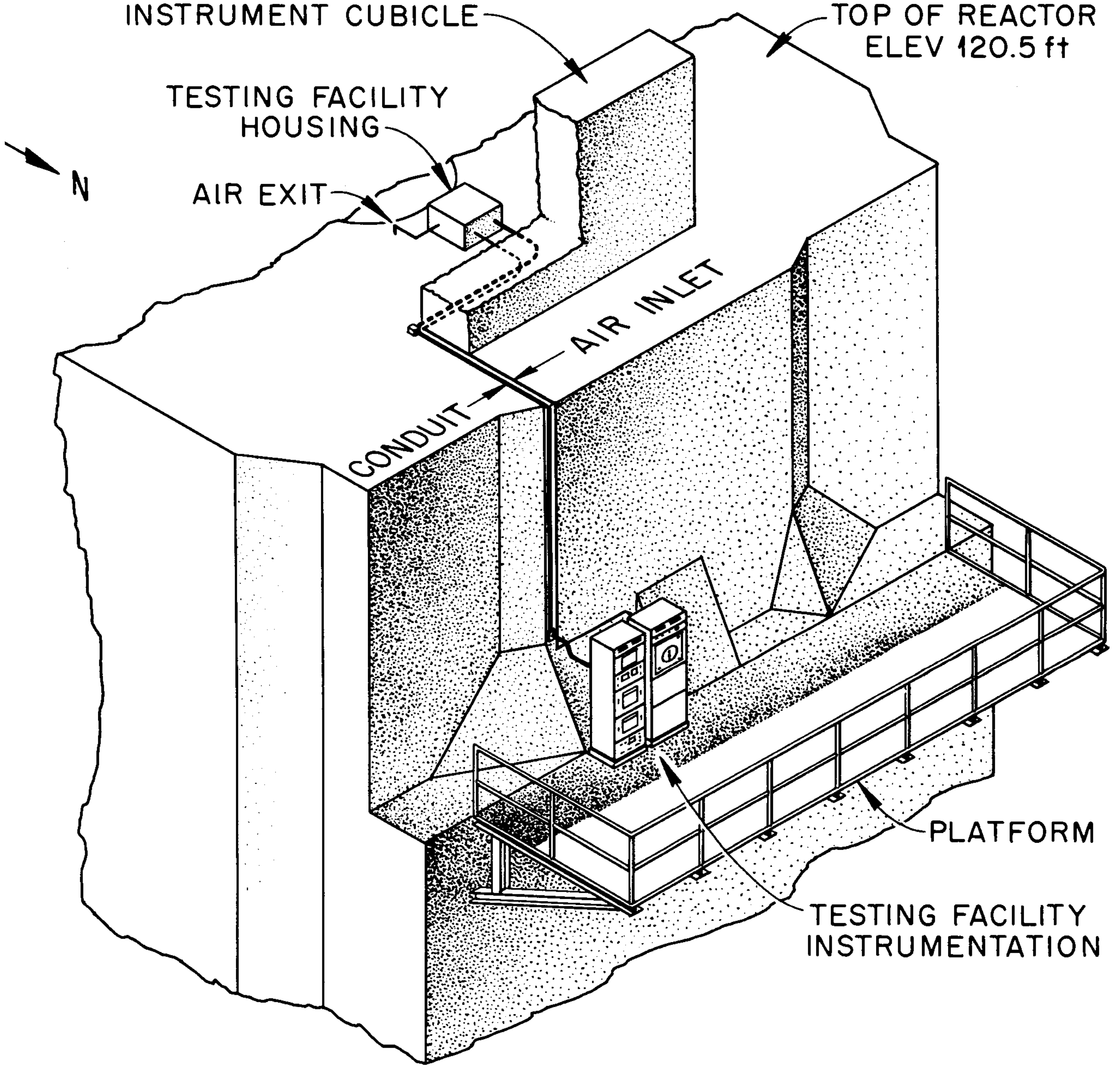

Fig. 2. Installation of Control Instrumentation for MTR Capsule Program.

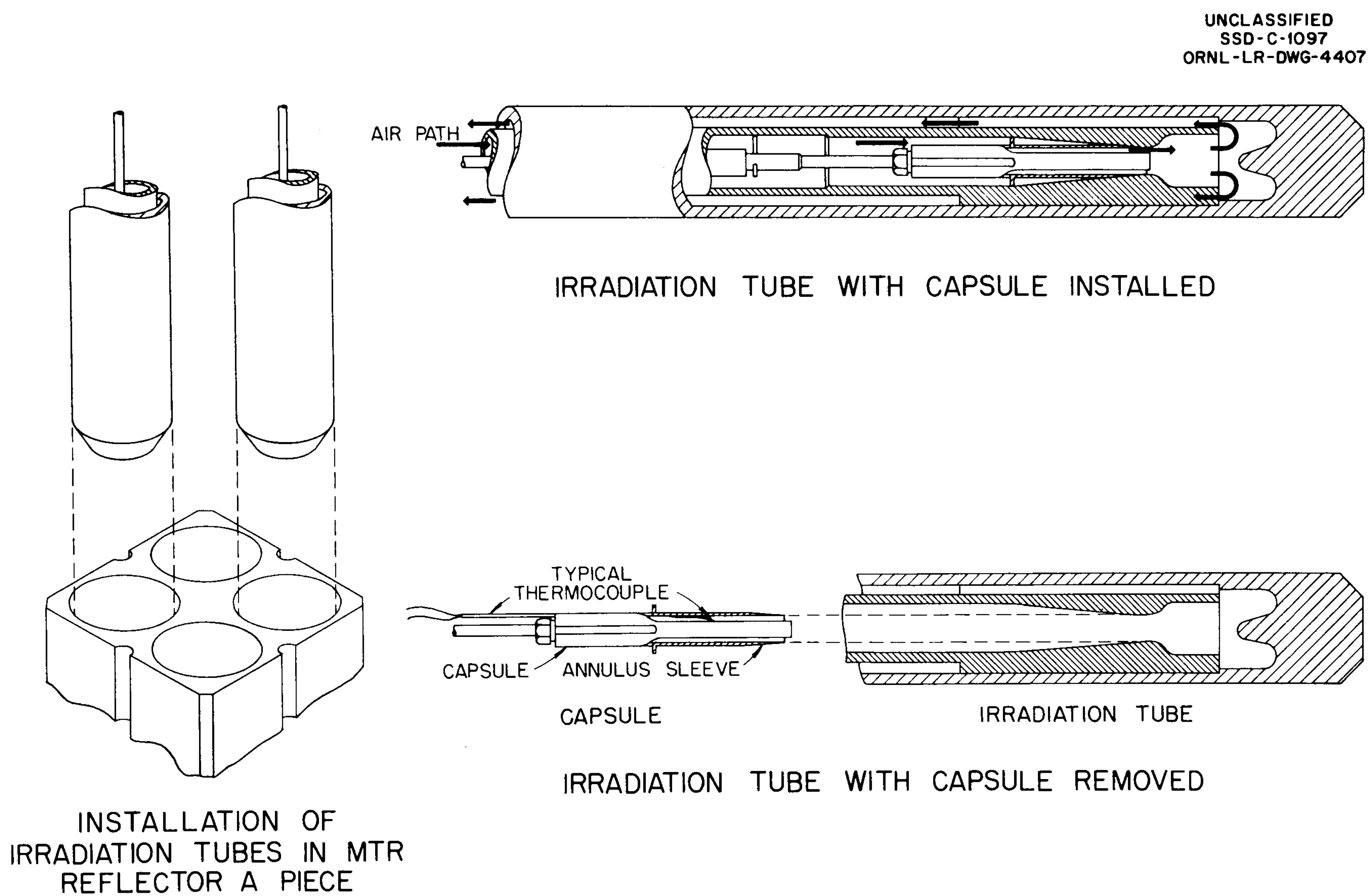

Fig. 3. Facility for Irradiation of Molten Fluorides in the MTR.

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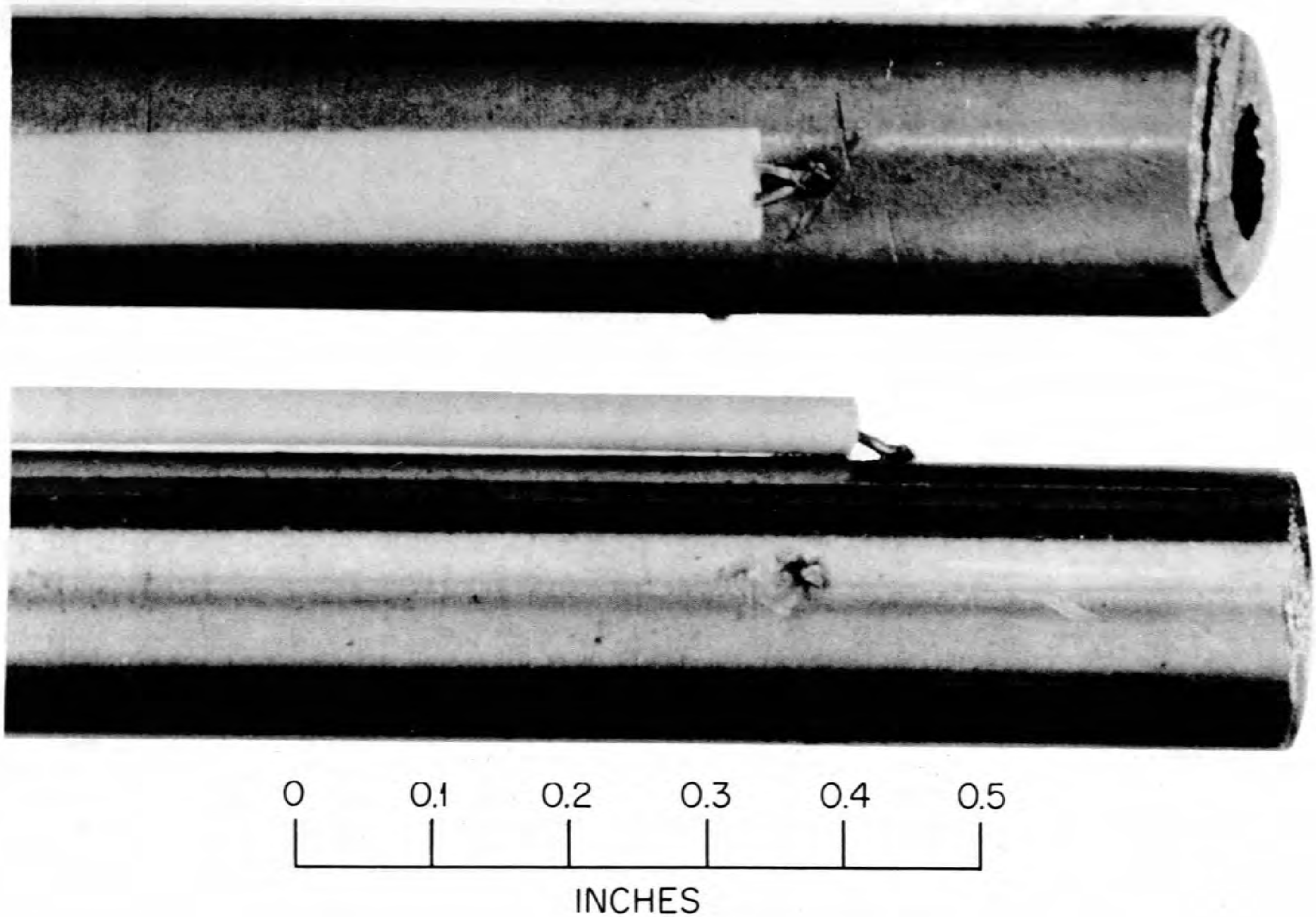
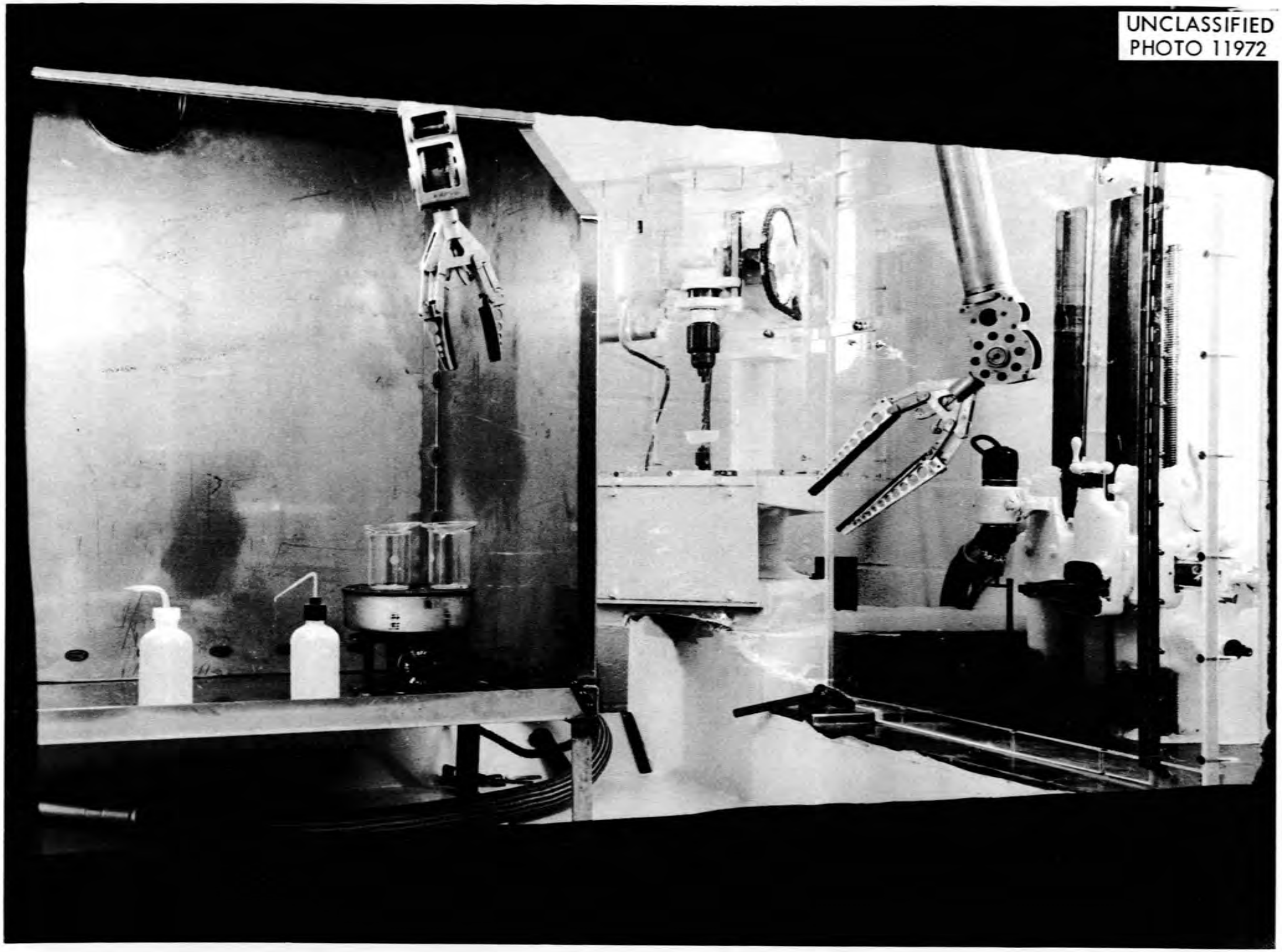


Fig. 4. Thermocouples for Use in High-Velocity Air Streams.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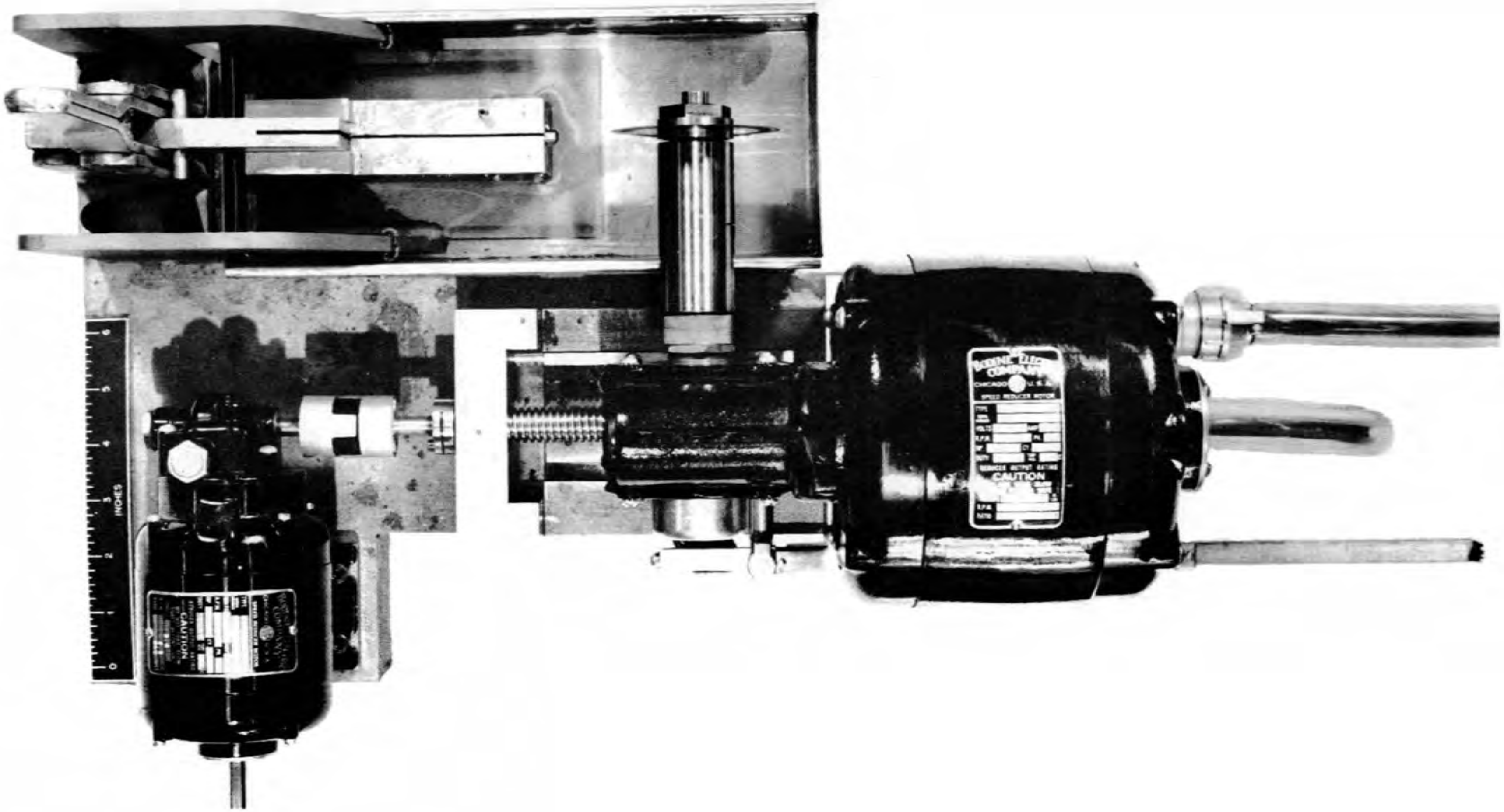

Fig. 6. Remotely Controlled Slitting Saw.

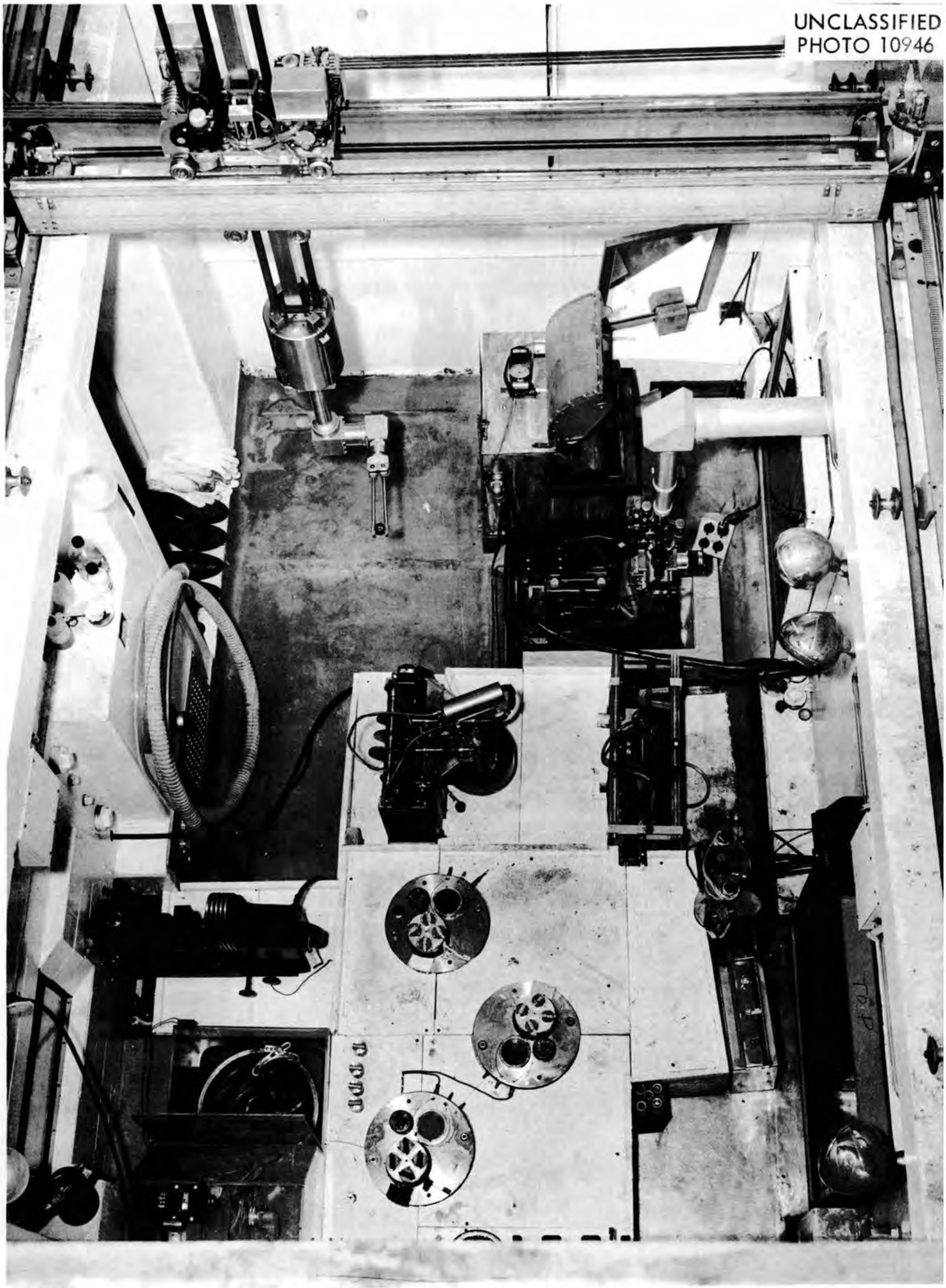

Fig. 7. Hot Cell Equipped for Preparing Metallographic Specimens.

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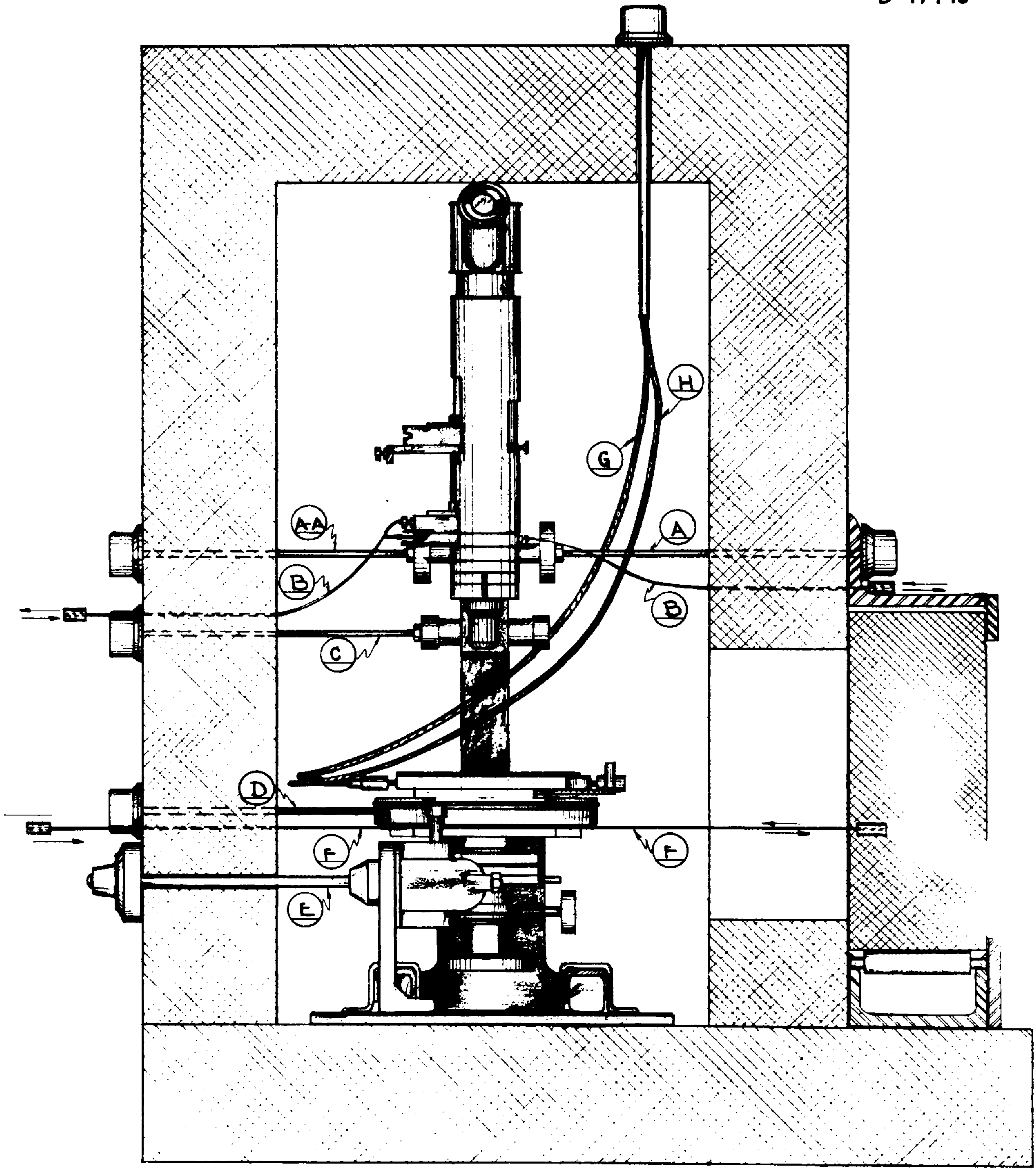

FRONT ELEVATION
[LEAD SHIELD CUT AWAY]

Fig. 8. Shielded Petrographic Microscope.

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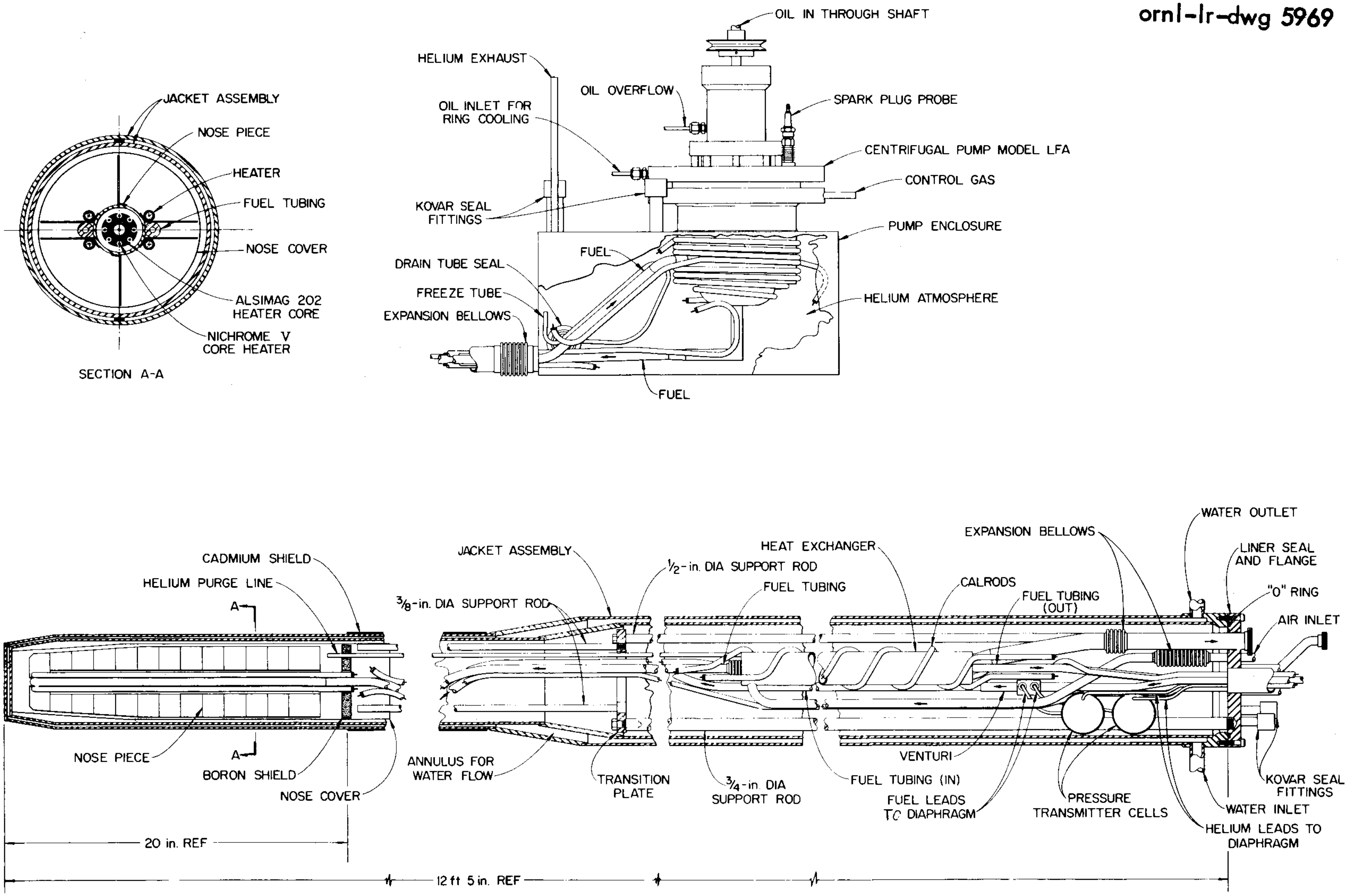

Fig. 9. LITR Horizontal Forced-Circulation Loop for Dynamic Corrosion Testing of Molten Fluorides.

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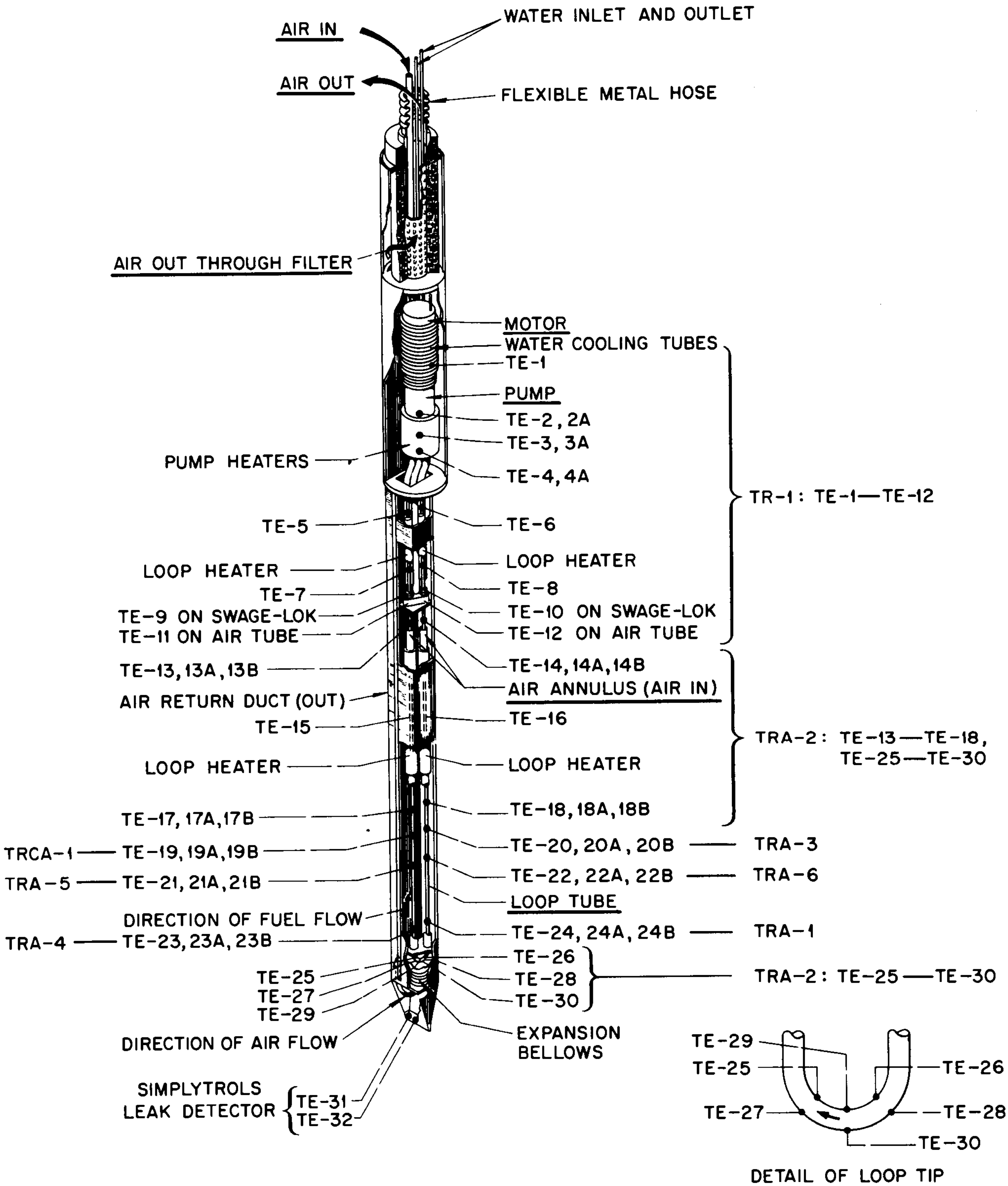

Fig. 10. LITR Vertical Forced-Circulation Loop for Dynamic Corrosion Testing of Molten Fluorides.

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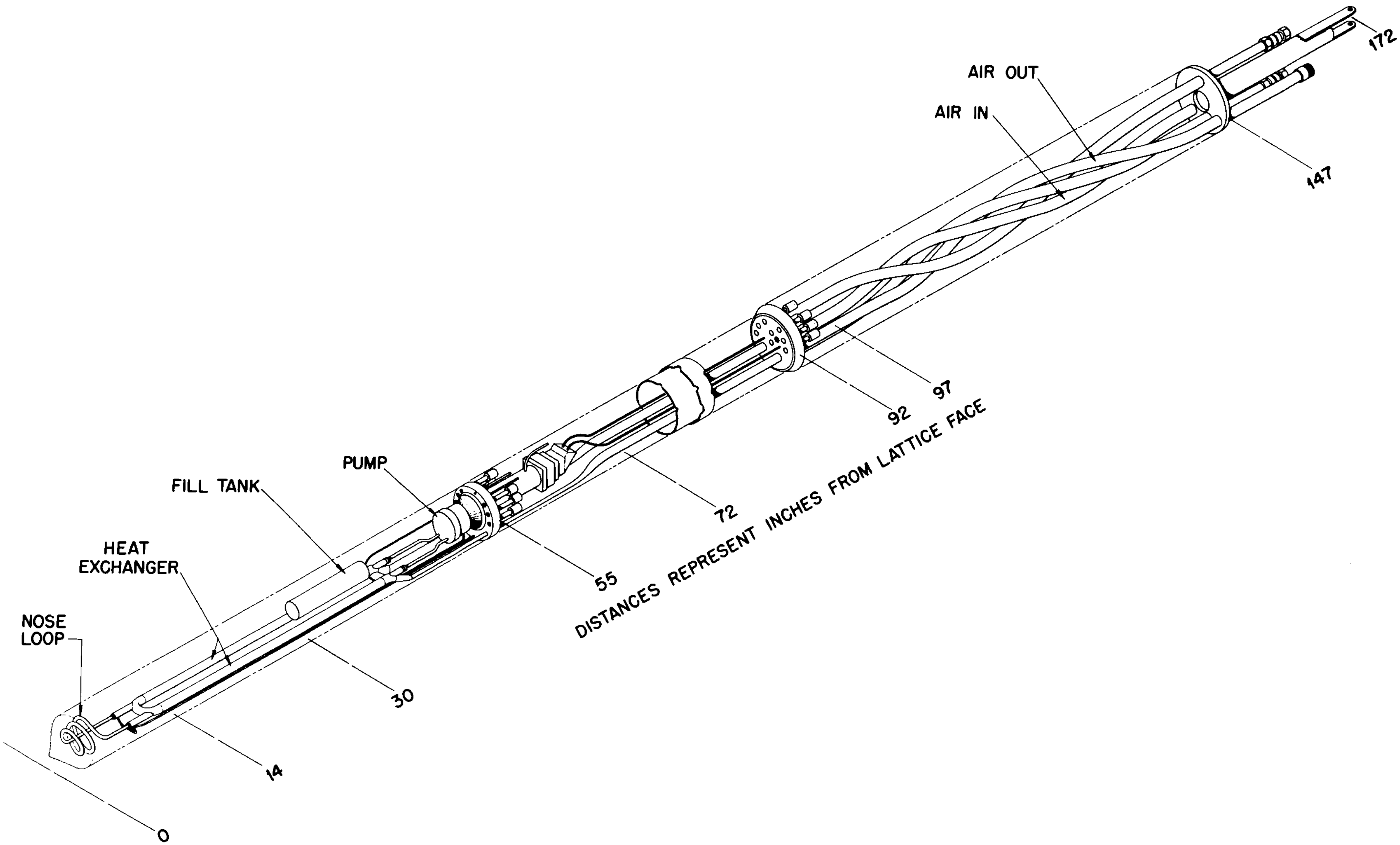

Fig. 11. MTR Horizontal Forced-Circulation Loop for Dynamic Corrosion Testing of Molten Fluorides.