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SEPARATIONS CHEMISTRY

QUARTERLY PROGRESS REPORT

SEPTEMBER – DECEMBER, 1956

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

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QUARTERLY PROGRESS REPORT
SEPTEMBER – DECEMBER, 1956

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ABSTRACT

Efforts during the quarter brought the hot cave to completion and it was used for remotely operated kilogram-scale oxide drossing experiments on uranium fuel. In addition, an experiment using 33 kg of uranium alloy was conducted to determine the scavenging effect of uranium carbide on zirconium, niobium, and molybdenum and to study tilt-pour casting.

The decontamination experiments involving fission product evaporation by arc melting have been directed toward the removal of fission products from irradiated thorium-uranium alloys and the determination of the protactinium loss from irradiated thorium.

The radiochemical analyses for the salt bed extraction experiments on irradiated thorium uranium alloy are nearing completion. The molten arc electrolysis efforts on thorium consisted of experiments to determine the properties of container materials, electrolyte composition, and cathode alloy.

This report is based on studies conducted for the Reactor Development and Research Divisions of the Atomic Energy Commission.

THE TWO PREVIOUS QUARTERLY PROGRESS REPORTS ARE:

NAA-SR-1697	April - June 1956
NAA-SR-1759	July - September 1956

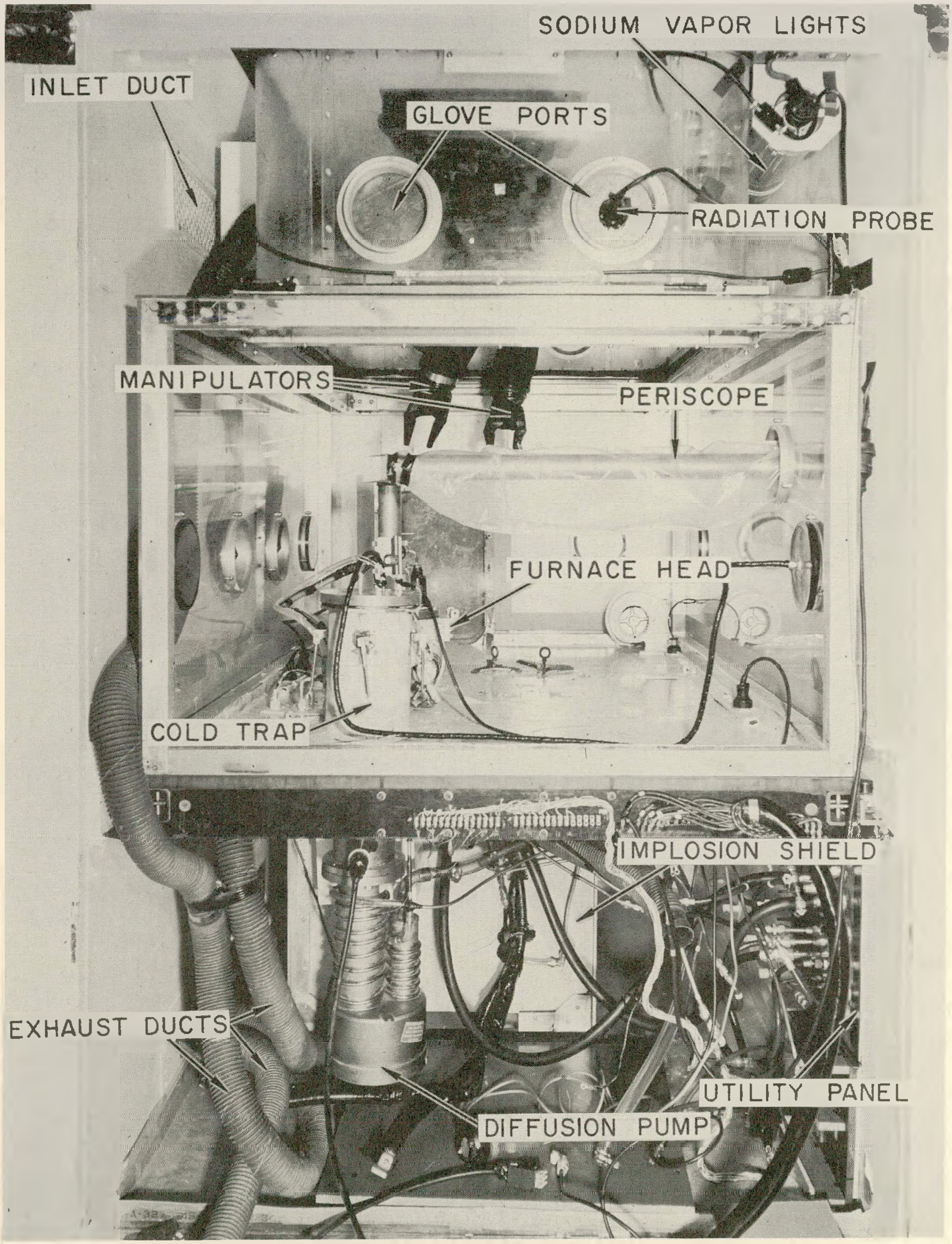

Fig. 1. View of Process Cave Showing Isolation Box and Service Connections

I. INTRODUCTION

The separations chemistry studies of high temperature methods of reprocessing nuclear fuels at Atomics International have been directed toward the development of pyrochemical methods for removing fission products and fissionable elements from metallic uranium and metallic thorium fuels. This report describes the current work on the kg scale pyroprocessing of uranium and progress on basic high temperature separations chemistry of thorium and uranium.

II. KILOGRAM SCALE HIGH TEMPERATURE PROCESSING METHODS FOR URANIUM FUELS

A. CAVE RECONSTRUCTION AND MODIFICATION (S. Strausberg, T. H. Mills)

During the past quarter the Process Initiation Unit's work brought the west cave sufficiently near completion to be used for remotely operated kilogram scale oxide drossing experiments.

The following process equipment items were completed:

1) Sectional masonite bench top
2) Upper and lower plastic boxes (remodeled)
3) Induction furnace assembly
4) Implosion shield
5) Vacuum system

This equipment is depicted in Fig. 1. The upper plastic box was attached to a heavy piece of aluminum which is fastened to the ceiling of the cave. The lower plastic box was mounted to the table top. During an experiment, these boxes are joined together by inflatable seals to form an air tight enclosure containing the main operational apparatus.

The remotely operated furnace assembly consists of a fused silica vacuum envelope, induction coil, furnace head, graphite crucible, and radiation shield. As a safety measure, the furnace assembly is enclosed in a transite implosion shield. The furnace assembly, implosion shield, and vacuum system were mounted to the table top. The electrical, water, and air connections were made to the utility panel.

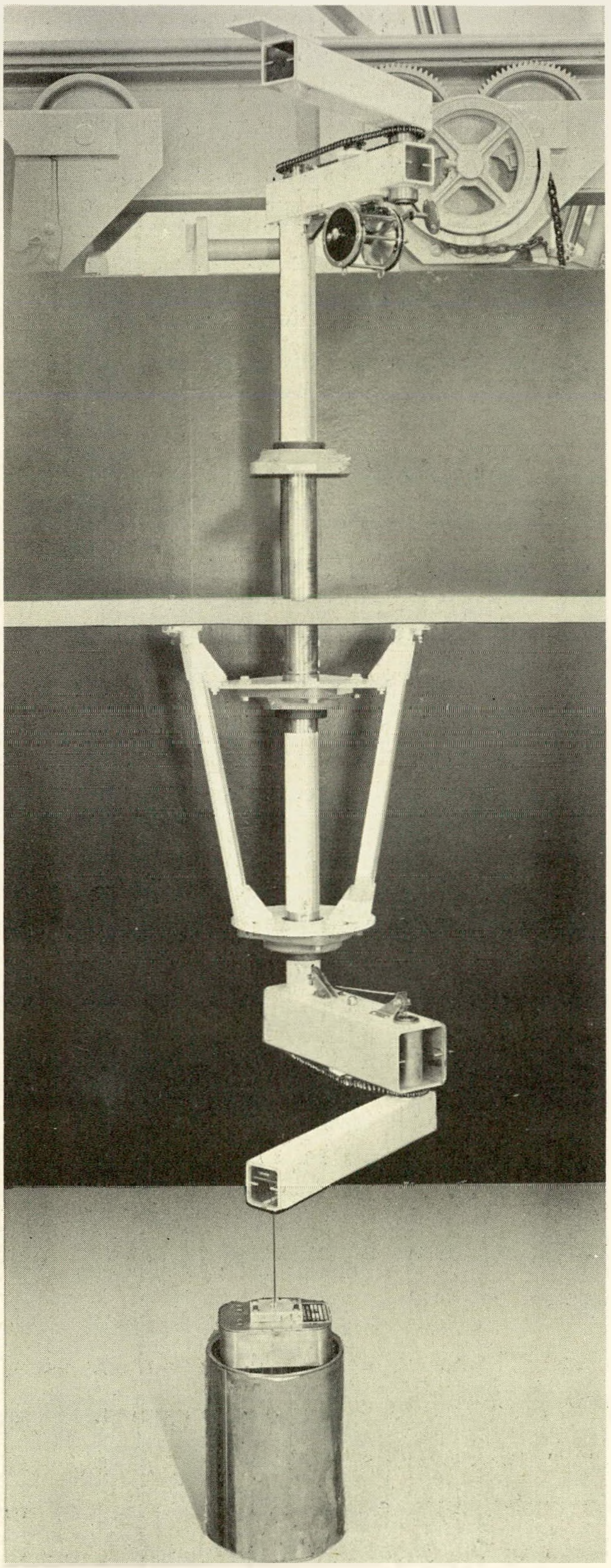

Fig. 2. The Testing of Transfer Cave Manipulator

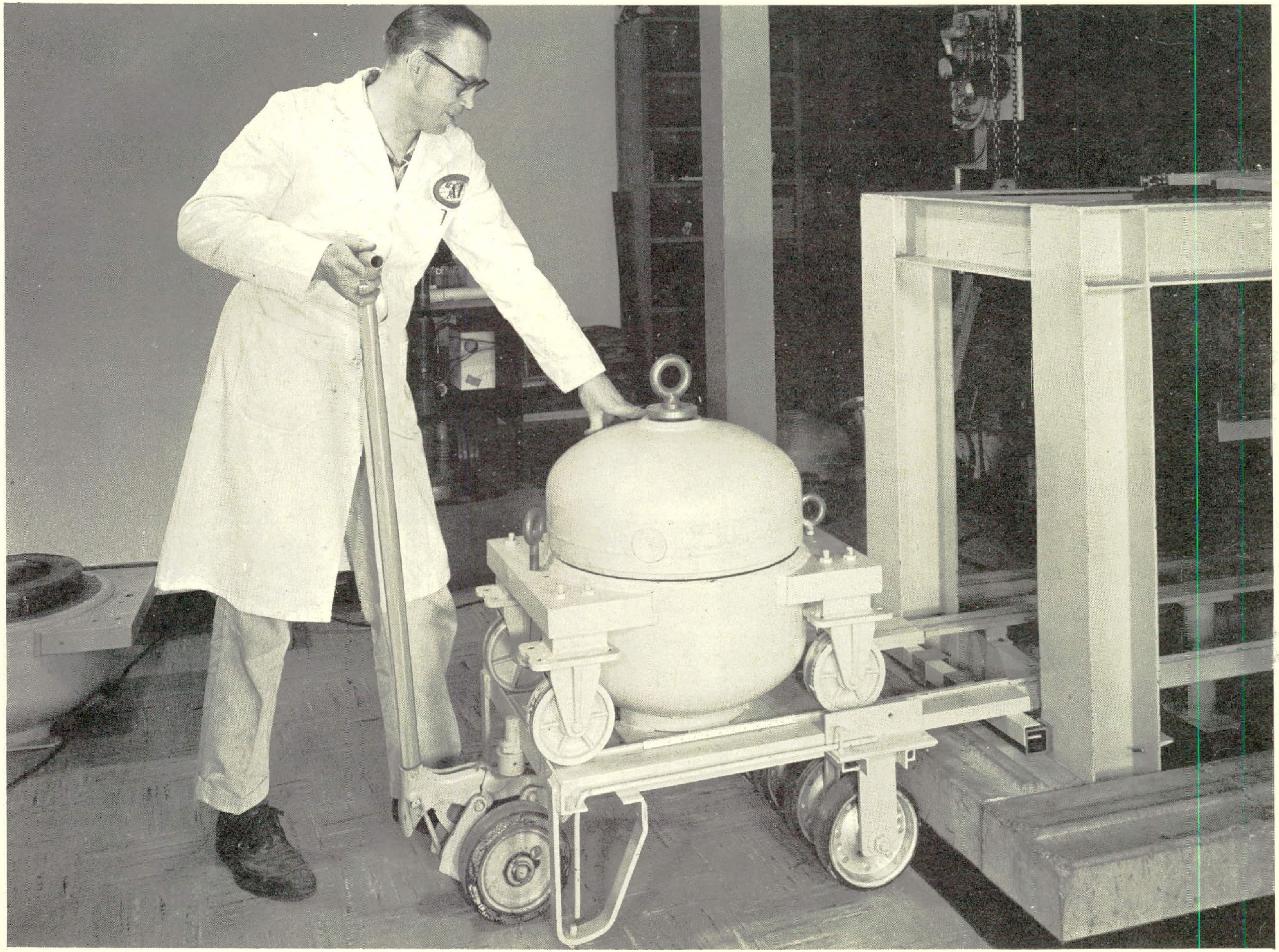

Fig. 3. The Loading of Transfer Cask Into Transfer Cave

A manipulator for transferring irradiated material was installed in the transfer cave interconnecting the two hot caves. Figure 2 is a photograph of this transfer manipulator. The transfer cask containing the can of irradiated material is rolled from a cart onto tracks inside the transfer cave. This is shown in Fig. 3. The cover of the cask is removed with a crane and the cask is moved along the tracks to a position under the transfer manipulator. An electromagnet is lowered until it contacts an iron ring fastened to the can containing the irradiated material. The can is then raised by the manipulator and may be transferred into either cave by swinging the manipulator arms which are controlled from the top of the transfer cave. The transfer manipulator is also used to transfer material from one cave to another.

B. CARBIDE SCAVENGING (J. Guon, T. E. Luebben)

An experiment was conducted to determine the scavenging effect of uranium carbide using the apparatus shown in Fig. 4. Thirty-three kilograms of uranium alloy (U = 99.2 per cent, Zr = 0.40 per cent, Mo = 0.2 per cent, and Nb = 0.1 per cent) were melted in a urania-coated magnesia crucible in the vacuum induction furnace. The molten uranium was stirred 30 seconds with a 3/4-inch diameter graphite rod and held at 1370° C for 5 minutes. The uranium was then poured into a tun dish containing twelve molds. Ten molds were made of graphite and two were made of steel. All molds had been coated with uranium oxide and outgassed at 350° C for 3 hours.

Photographs of these slugs are shown in Fig. 5 and 6. The slugs were broken from their risers at liquid nitrogen temperatures, the flash machined away, and each end slightly beveled. The diameter and bow of the slugs were measured and the results tabulated in Table I.

The surfaces of the slugs cast in graphite were rough and dark, while those cast in steel were relatively smooth and shiny. All slugs had some shuts, surface inclusions, and evidence of porosity. The 1/2-inch and 5/8-inch diameter funnel produced slugs of comparable quality. There was no significant variation in the quality of slugs cast in molds located various distances from the distributor. Samples have been sent to the laboratory for analysis.

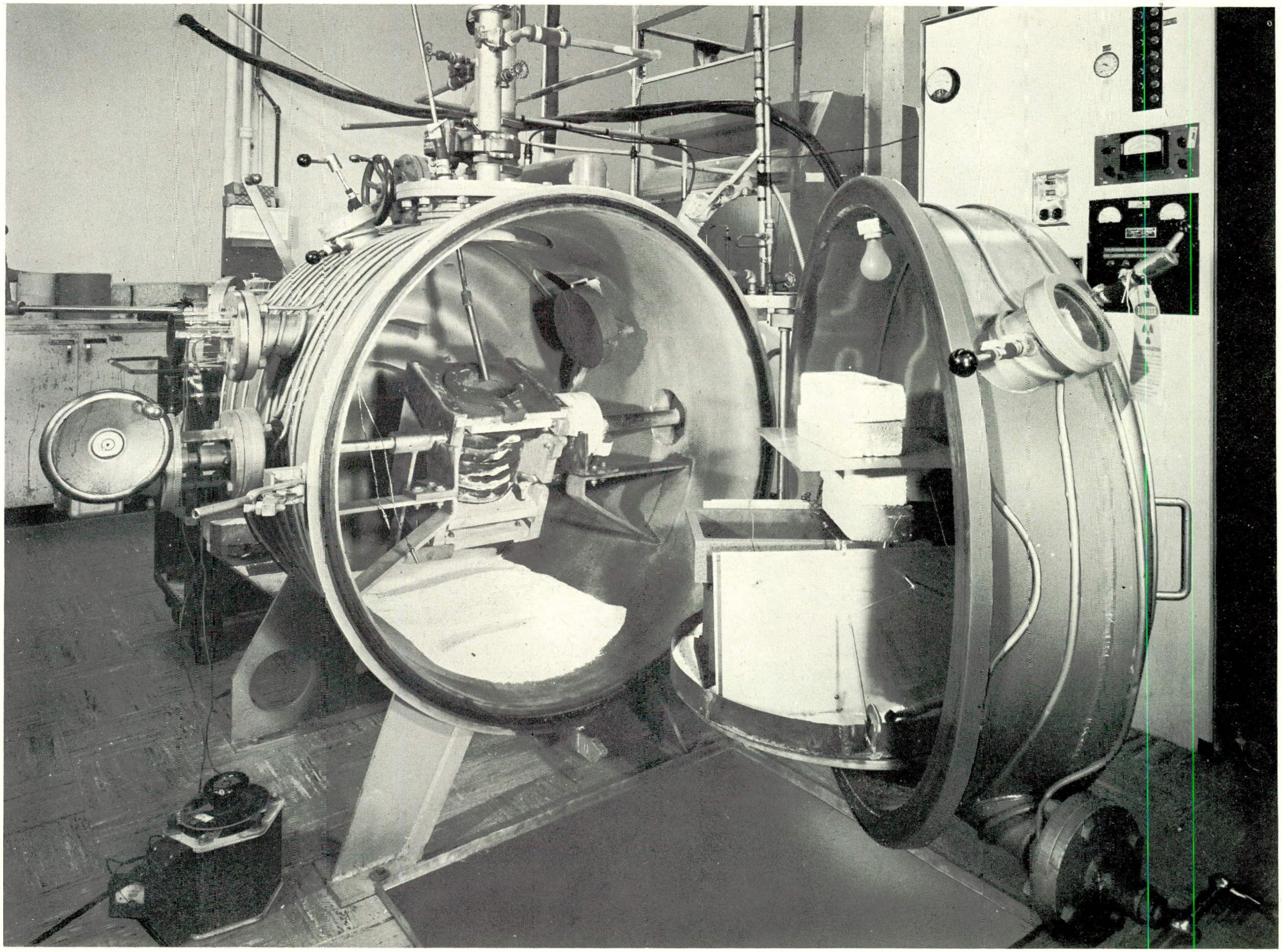

Fig. 4. Interior View of 50 Kg Vacuum Melting Furnace

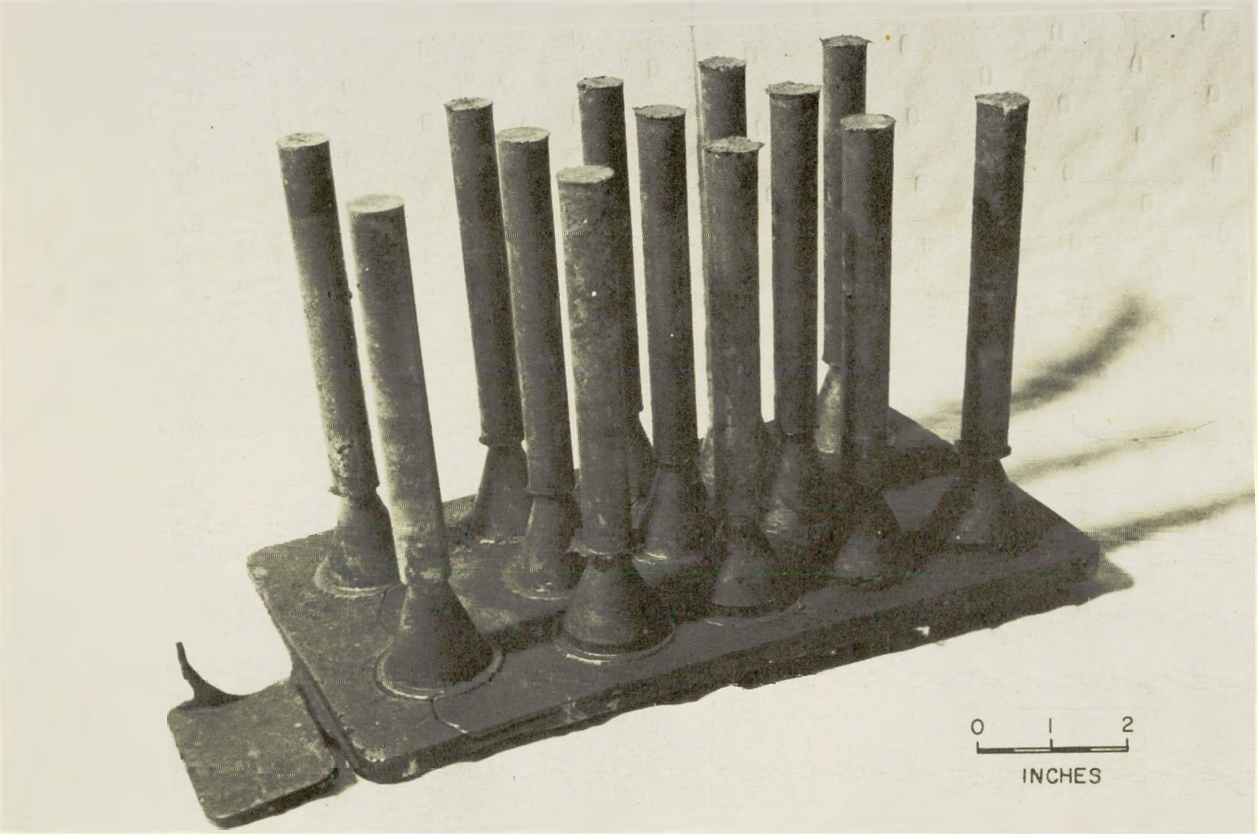

Fig. 5. Stripped Uranium Casting

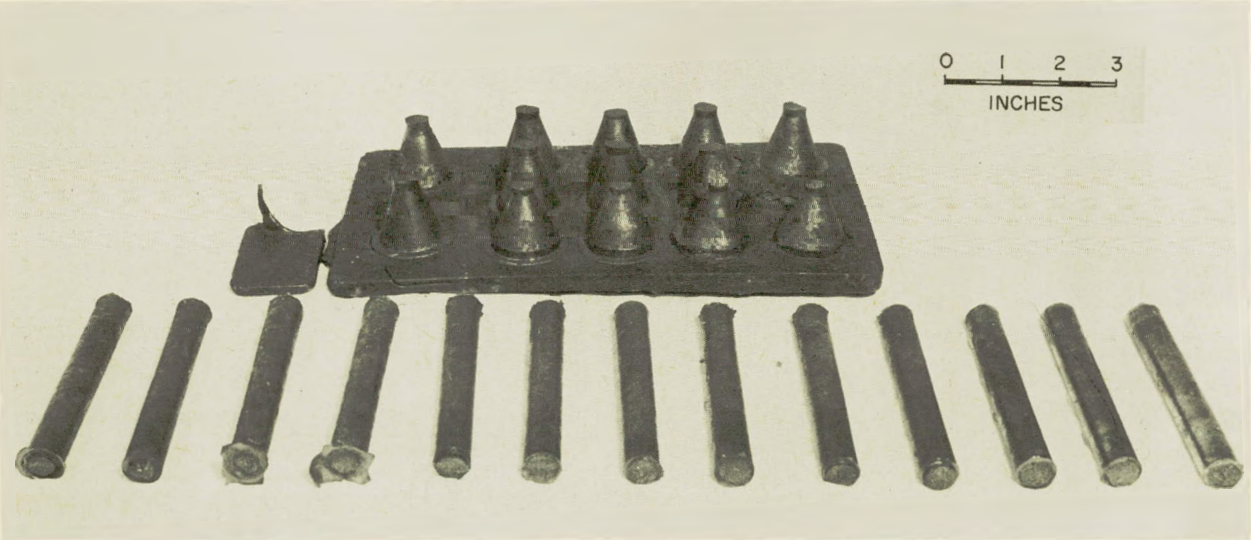

Fig. 6. Uranium Slugs Separated From the Gate

TABLE I

SLUG INSPECTION DATA

Slug No.	Funnel Diameter (Inch)	Diameter (inches)			Bow (mils)	
		End	Middle	Near Riser	Minimum	Maximum
1	1/2	0.751-8†	0.745-8	0.743-4	2.5	9.
2	1/2	0.750-4	0.740-1	0.743-5	2.	13.
3	1/2	0.752-5	0.736-9	0.748-52	7.	22.
4	1/2	0.753-6	0.742-4	0.742-5	10.	20.
5	5/8	0.759-62	0.742-5	0.740-3	**	**
6	5/8	0.747-52	0.740-2	0.744-2	1.5	16.
7	5/8	0.753-5	0.737-9	0.744-7	6.	15.
8	5/8	0.743-7	0.739	0.754-7	4.	14.
9	5/8	0.745-7	0.740-1	0.744-6	3.	14.
10	5/8	0.745-7	0.742-3	0.742-4	8.	9.
11	5/8	0.745-7	0.741-2	0.753-6	11.	14.
12*	5/8	0.766-7	0.764	0.764-5	††	9.
13*	5/8	0.768-9	0.763-4	0.765-6	††	16.

*Steel molds 0.788-in. ID, graphite molds 0.765-in. ID
†0.751 to 0.758 typical of values, due to hourglass shape
**Too badly hourglassed to be measured
††Effect of bow greater than hourglass

III. HIGH TEMPERATURE SEPARATIONS CHEMISTRY OF URANIUM

A. MECHANISMS OF FISSION PRODUCT EXTRACTION — URANIA DROSSING (T. Smith)

Uranium oxide drossing offers a means of removing fission products from irradiated uranium fuels. A preliminary investigation to determine the mechanism of this extraction has been undertaken. During the past quarter, this investigation was directed toward a study of the rate of cerium extraction by urania and the diffusion of cerium in molten uranium and in solid uranium.

1. Rate of Cerium Extraction by Uranium Dioxide - The vacuum apparatus Fig. 7 to be used for determining the effect of stirring on the rate of cerium extraction by UO_2 was completed. In this experiment a rotating cylinder of uranium dioxide is immersed into molten uranium containing radioactive cerium. The extent of reaction with the UO_2 phase is determined by taking samples of the uranium dioxide cylinder. An alloy of U-(0.01w/o)Ce^{141} was prepared and a urania drossing experiment carried out. Radiochemical analysis will be used to determine the extent of the reaction.

2. Cerium Diffusion Into Molten Uranium - In a series of diffusion experiments "tracer-spiked" cerium was melted in a resistance furnace and the temperature held constant for two hours. Samples taken at various depths will be used to determine the rate of diffusion of cerium in molten uranium.

The "tracer-spiked" cerium was prepared by placing 1/2 cc of an HCl solution of radioactive (Ce^{141}) $CeCl_3$ and 4.9 mg of sodium in a hole drilled in a piece of natural cerium weighing 2.121 gm. The cerium was then melted in an induction furnace and samples taken at various points in the resulting button. The results of these analyses are shown in Table II.

TABLE II

DISTRIBUTION OF CERIUM-141 IN CERIUM BUTTON

Sample No.	Position in Ce Button	Ce (cpm/mg)
1	Inside	4,630
2	Inside	6,860
3	Inside	4,520
4	Surface	11,400
5	Center	5,130

Although the radioactive cerium remained concentrated at the surface, this cerium mixture will be adequate for diffusion studies.

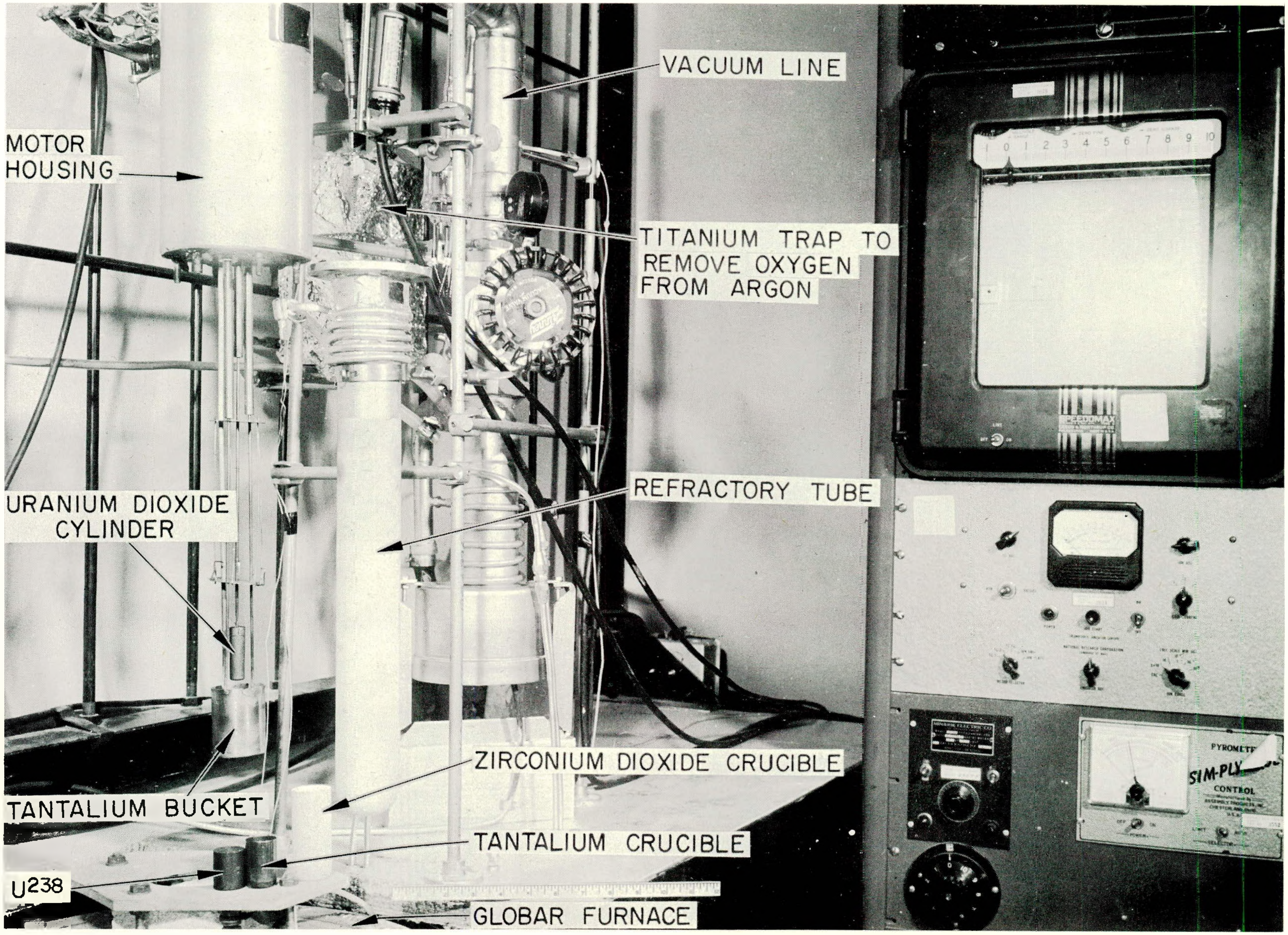

Fig. 7. Vacuum Apparatus for Mechanism Study

Using the Ce-Ce^{141} tracer, ten standards were made by dissolving the amount of cerium and uranium in HNO_3 that would simulate actual samples which could be expected from oxide drossing. Radiochemical analyses of these standards gave an average of 13,200 cpm/mg cerium and an average deviation of ± 5 per cent. These standards will be used for comparison when analyzing for cerium.

Two methods of analyzing for cerium have been studied, a colorimetric method developed by Hure and Saint James[1] and a radiochemical method described by Ballou.[2] The lower limit for the determination of cerium by the colorimetric method was 5γ/cc and the lower limit for the radiochemical method was 10γ/cc.

IV. HIGH TEMPERATURE SEPARATIONS CHEMISTRY OF THORIUM

High temperature separations studies concerning the removal of fission products from irradiated thorium-uranium alloy have been directed toward the development of three techniques: evaporation by arc melting, salt bed equilibration, and electrorefining from molten salt baths.

A. EVAPORATION OF FISSION PRODUCTS BY ARC MELTING (E. W. Murbach)

Experiments have continued on the removal of fission products from irradiated Th-U alloy by the arc-melting technique. One more sample in the series started during the previous quarter has been melted. Radiochemical analyses have been completed on a number of the induced activities. These data reveal that arc melting 2 to 3 grams of irradiated Th-(10w/o)U at 1850 ± 50° C for 2 to 8 minutes will remove 98 to 99 per cent strontium, 31 to 98 per cent cerium and rare earths, some zirconium, protactinium and uranium, and only traces of niobium.

As a first approximation, the amount of niobium present in the samples was calculated from measured zirconium activities. From previous irradiation history of the sample and cooling time, the calculation can be made in a straightforward manner by using the radioactive decay laws. The results obtained from this calculation indicated substantial loss of protactinium from some of the samples.

In an attempt to provide for better analytical data a modified procedure was developed. A sample of the solution was treated with an equal volume of

0.5 M TTA in benzene. According to Moore,[3] zirconium and protactinium are almost quantitatively extracted in one contacting. The organic phase was wet-ashed with concentrated HNO_3 and the protactinium determined by carrying on MnO_2, as the activity of the solution is too low to make direct counting of an aliquot satisfactory. Niobium was then determined using MnO_2 as the carrier.

One of the elements to be considered in irradiated thorium pyroprocessing is protactinium. The presence of protactinium should be determined precisely. With this thought in mind a sample of thorium metal was irradiated to a flux of approximately 4 x 10^{13}. To date one sample has been arc melted for 4 minutes at approximately 1900° C. The first analytical result indicates a loss of protactinium of about 10 per cent.

B. FISSION PRODUCT EXTRACTION BY SALT BED PROCESSING (A. G. Buyers)

No further equilibration experiments for thorium-uranium fused halide melts were carried out during this quarter. This period was spent in completing radiochemical evaluation of previous runs. New available data are presented in Table III.

TABLE III

SALT BED PROCESSING EMPIRICAL DATA
IRRADIATED Th-U 10 PER CENT ALLOY CaF_2 SALT COLUMN

Bed Length (Inches)	Heating Period (Minutes)	Th Loss (%)	Per Cent Removal				
			R.E.	Ce	Cs	Pa	Sr
1	3	1.4	37*	35*	35*	7*	59*
1-1/2	5-1/2	2.4	73*	75*	45*	7*	70*
2-3/4	10	4.3	75	84	--	11	62
4-1/2	16	8.6	95	96	78	13	95
6-1/8	28	11.6	--	98	92	13	97

*Previously Reported

C. ELECTROREFINING OF THORIUM IN MOLTEN HALIDE BATHS

(W. N. Hansen)

Fundamental problems considered in attempting to develop a successful method for electrorefining thorium by the "dripping cathode" method are: 1) determining suitable cathode metal and obtaining suitable cathode metal in desired form; 2) determining a suitable container for molten electrolyte and for molten alloy or for both together; and 3) determining a suitable electrolyte. These problems are interdependent and have therefore been carried along together. For discussion they will be taken separately in the order given.

1) Low melting alloys of Th-Mn and Th-Fe melting at ca., 911° C and ca., 860° C respectively have been reported.[5] From the standpoint of recovery of pure thorium by vaporization of the alloying metal manganese should be superior to iron because of its higher vapor pressure. Because of the brittle nature of manganese metal it is not generally available in rod form suitable for making a cathode, and it was necessary to cast the manganese in the desired form. Zirconia, recrystallized alumina, and tungsten were found satisfactory for casting the metal. Porcelain, fused quartz, magnesia, porous alundum, graphite, molybdenum, and platinum were found unsatisfactory.

   Because it is readily available and more convenient to use, iron was used as a cathode while investigating subjects of 2) and 3) above. It was found that satisfactory alloying was obtained with an iron cathode when the electrolysis cell was held at ca., 1000° C, this being ca., 150° C above the melting point of the eutectic.

2) Graphite has been used as a container in the electrorefining of uranium by the present method.[6] It was found in this laboratory, however, that manganese reacts readily with graphite at temperatures near 1000° C. This indicates that graphite will probably not contain the Th-Mn alloy near 1000° C without contaminating the alloy with carbon. Molten manganese at ca., 1300° C was found to dissolve tantalum only slowly (the diameter of

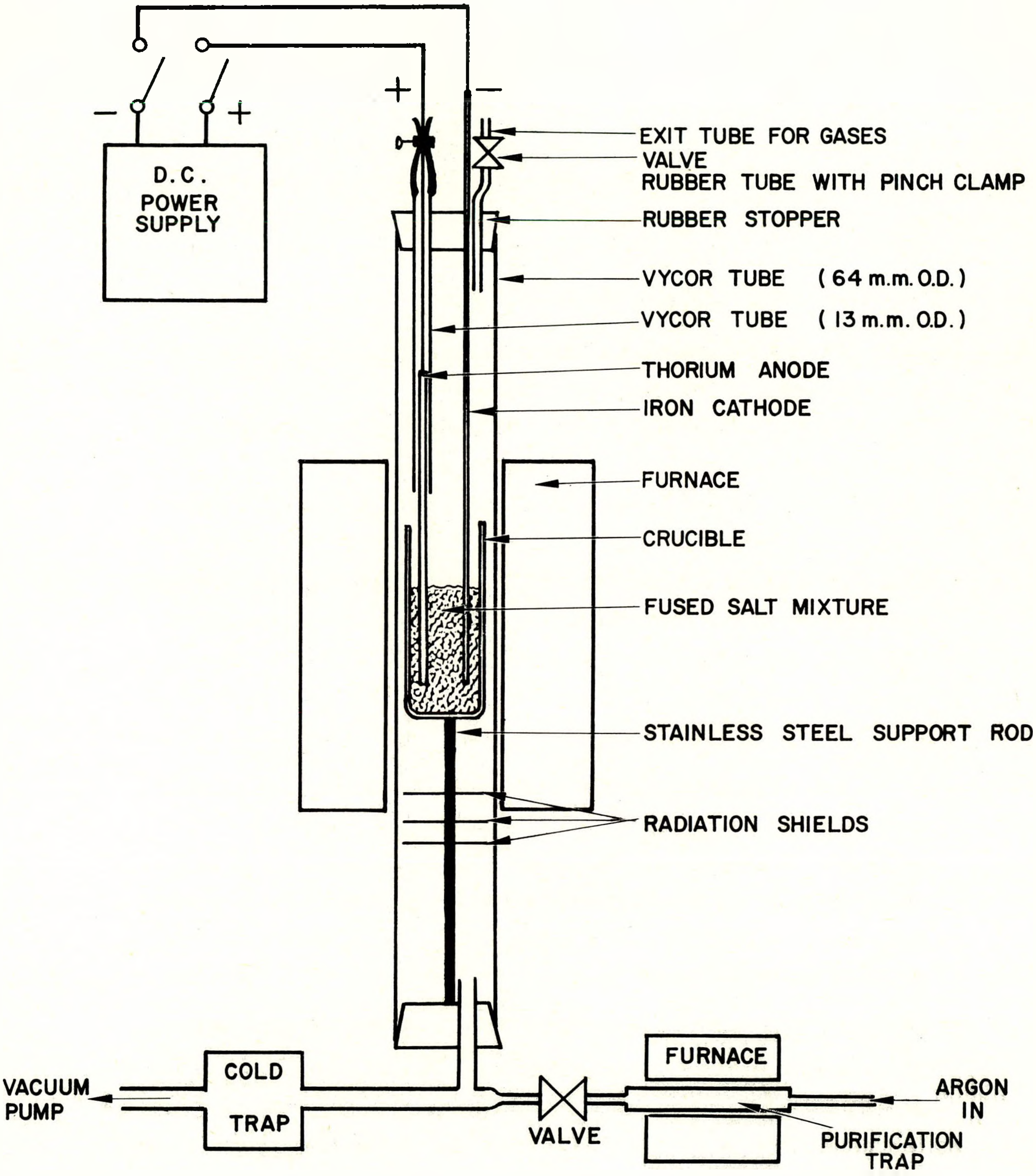

Fig. 8. Apparatus for Electrorefining Thorium in Fused Halide Baths

TABLE IV

ELECTROREFINING OF THORIUM FROM MOLTEN HALIDE BATHS

Run	Salt Mixture	Cathode	Crucible Material	Temp. (°C)	(Volts)	(Amps)	Remarks
10-1	100 gm NaCl 100 gm $ThCl_4$	tantulum wire (area = ca., 1 cm^2)	stabilized zirconia	835	1.0	0.7	Thorium was deposited on cathode as crust of finely divided metal. Bath volatilized, collecting as dust throughout apparatus (this was true with all runs using $ThCl_4$).
10-2	as in 10-1	small piece of Mn (ca., 1 cm^2) held by Ta wire	as in 10-1	955	1.0	0.6	Deposit was essentially as in run 10-1; no significant alloying with Mn occurred at this temperature.
10-3	as in 10-1	1/4 in. OD iron rod (ca., 10 cm^2)	as in 10-1	1010	1.0	2.0	Alloying with iron occurred and a drop formed on bottom of rod; some dendritic growth also formed.
10-4	200 gm NaCl 2 gm $ThCl_4$	as in 10-3	as in 10-1	1000	1.0	0.5	Drop of alloy formed; very little dendritic growth; large quantities of Na were formed.
10-5	MgF_2-46 gm CaF_2-34 gm ThF_4-20 gm	iron rod with ca., 5 cm^2 area	graphite	1050	1.0	0.27	Drop of alloy formed; no dendritic deposit; magnesium formed and distilled from bath.
10-6	ThF_4-10 M/o LiF_4-90 M/o	as in 10-5	nickel	1000	0.2	0.5	Th-Fe alloy was formed and dripped into bath. Bath was stable and non-volatile.

1 mm wire decreased ca., 10 per cent in 10 min). A tungsten wire was not affected by molten manganese. Molybdenum and platinum were completely dissolved. It appears that tantalum will be a possible container for Th-Mn alloy in the presence of fused salts. This remains to be confirmed as does the reactivity of Th-Mn alloy with graphite at 1000° C.

Graphite was found to be a satisfactory container for MCl_x-$ThCl_4$ and MF_x-ThF_4 electrolytes (M being an alkali or alkaline earth metal). Zirconia was found to be satisfactory for NaCl-$ThCl_4$.

3) The apparatus shown in Fig. 8 was constructed, and electrolysis experiments conducted using NaCl-$ThCl_4$ as the electrolyte with an iron cathode. The salt bath was volatile at 1000° C in spite of the atmosphere of argon. Except for volatility, a 50 (w/o $ThCl_4$)-NaCl electrolyte gave satisfactory performance.

An electrolysis experiment was carried out using a 10(w/o)ThF_4 mixture with LiF and a molten Th-Fe alloy was formed at the cathode. This bath was found to be satisfactory since it possessed high stability and low volatility. Experiments also indicate that a bath composed of ThF_4, CaF_2, and LiF could be used. Results of electrolysis experiments with electrolytes of various composition are given in Table IV.

SUMMARY

The reconstruction of the hot cell and in-cell equipment has been sufficiently completed to permit remotely operated oxide drossing experiments to be carried out. An experiment was conducted on 33 kg of uranium alloy to determine the scavenging effect of uranium carbide on zirconium, niobium, and molybdenum. Casting studies were made in connection with this experiment.

An investigation of the chemical mechanisms for fission product extraction resulting from irradiated uranium-urania contacting has been initiated. Preliminary interests were directed toward producing a homogeneous, Ce-Ce^{144} + U alloy and checking analytical procedures.

Thorium decontamination experiments involving evaporation by arc-melting of irradiated thorium-uranium alloy have shown nearly complete strontium removal; intermediate cerium and rare earth evaporation; erratic distillation of zirconium, protactinium, and uranium; and negligible removal of niobium in 2 to 8 minutes.

Salt bed processing experiments, using irradiated thorium-uranium alloy, calcium fluoride beds, and heating for periods of 16 to 28 minutes, have shown greater than 90 per cent removal of cerium, rare earths, tellurium, and strontium.

The execution of a successful experiment designed to remove fission products from irradiated thorium-uranium alloy by electrolysis in fused halide baths has depended upon solution of these preliminary problems: selection of cathode metal, container materials, and electrolyte. An iron cathode was found to form a dripping alloy at 1050° C during the electrolysis of thorium-uranium alloy in a molten ThF_4-LiF bath contained in graphite. It is suggested that iron carbide may form in the product alloy upon contact with graphite and that a better electrolyte could be ThF_4, CaF_2, and LiF.

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