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# SEPARATIONS CHEMISTRY
# QUARTERLY PROGRESS REPORT
# APRIL - JUNE, 1957

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NAA-SR-2168
CHEMISTRY-SEPARATION PROCESSES
FOR PLUTONIUM AND URANIUM
37 PAGES

# SEPARATIONS CHEMISTRY

## QUARTERLY PROGRESS REPORT

## APRIL – JUNE, 1957

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## ABSTRACT

A scale-up experiment was carried out to study the plutonium extraction from molten uranium by uranium fluoride. No analytical data is available at this time, but the proceedure and apparatus are described.

A test operation in which six irradiated slugs were cold-short fractured is described. The spread of contamination resulting from this operation was very small.

The analytical results of a previous kilogram-scale oxide-drossing experiment show the following fission-product removals: 98 per cent cesium and cerium, 95 per cent tellurium, over 99 per cent rare earths and strontium, and 1 per cent ruthenium.

Studies undertaken to determine the mechanism of fission-product extraction by oxide drossing show the solubility of cerium in molten uranium to be 2 per cent. The results of experiments in which uranium-cerium alloys were oxide drossed with zirconia and magnesia indicated cerium oxide concentrates in the uranium metal near the metal-oxide interface.

The results of investigations in which irradiated thorium-uranium alloys were melted and held at temperatures several hundred drgrees above the melting point show that the evaporation loss of protactinium is from 24 to 36 per cent and that of uranium is up to 14 per cent.

An experiment is described in which a thorium-uranium alloy was drip-induction melted. Experiments undertaken to determine the solubility of thorium in molten zinc are described.

The results of an electrolysis experiment in which irradiated Th-10 w/o U was electrorefined using a molten salt bath and a liquid zinc cathode showed that 58 per cent of the zirconium, 79 per cent of the cerium, 84 per cent of the rare earths, 91 per cent of the ruthenium, and greater than 99 per cent of the strontium and cesium were removed.

Experiments are described in which irradiated Th-10 w/o U was melted by induction heating and allowed to melt through frozen calcium fluoride. The results of these investigations show that greater than 80 per cent of the cesium, strontium,

and tellurium are removed. Ruthenium, protactinium, zirconium, and uranium losses were negligible. Thorium losses to the salt bed approached 12 per cent.

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

# I. INTRODUCTION

Research and development studies concerning high temperature methods for processing nuclear fuels have been directed toward the development of pyrochemical methods for removing fission products and fissionable elements from thorium reactor fuels. This report describes the progress on the scale-up pyroprocessing methods and the investigations of high-temperature separations chemistry of thorium and uranium.

# II. PROCESS INITIATION EFFORTS ON THE PYROPROCESSING METHODS FOR URANIUM FUELS

## A. EXTRACTION OF PLUTONIUM FROM MOLTEN URANIUM BY FUSED URANIUM FLUORIDE (T. Luebben, T. Mills and J. Roberts)

An experiment was carried out to study the extraction of plutonium from the molten uranium by fused uranium fluoride. Uranium which had most of the fission products removed by oxide drossing was used for this experiment.

A plutonium extraction experiment was conducted in the Hot Caves. A 2:1 metal-salt ratio consisting of 517.5 gm of uranium and 258 gm of $UF_4$ powder (minus 300 mesh) was placed in a graphite crucible. This crucible was surrounded by a cylindrical 10-mil tantalum radiation shield inside of a graphite shield. The crucible and graphite shield were equipped with carbon lids. Titanium disks, 25-mils thick, were placed immediately above and below the graphite shield. The crucible exterior and the entire graphite shield were covered with magnesium zirconate wash. The system was outgassed at a vacuum of 28 inches of mercury gage and flushed 10 times with helium. The last three flushes were carried out at a charge temperature of approximately 1000° C. After flushing was completed and the helium pressure was adjusted to 20 inches of mercury absolute, the power level was gradually raised to obtain a charge temperature of 1410° C; this temperature was held for one hour.

Conditions during the major part of the operation were as follows:

1) Pressure - 28 inches of mercury absolute,
2) Temperature - 1360° C as read, 1410° C as estimated,
3) Holding time - one hour at 1410° C.

During this time the pressure rose to 28 inches of mercury absolute and remained thus until the power was shut off, then it dropped back to 21 inches of mercury absolute.

The furnace top and interior were dismantled in a "glove bag" to avoid any external scattering of contamination. The bag is constructed of clear vinyl sheet, and is provided with gloves as an intrinsic portion of the bag. These gloves are fastened and sealed to the sheet by means of pressure-sensitive cellulose-acetate tape.

Examination of the furnace interior showed that a heavy film, green in some portions and buff in others, had formed during the operation. A similar furnace coloration was observed on fusing $UF_4$ in a graphite crucible with no other materials present.

The melt was surrounded by a smooth skull and separated easily from the crucible. The salt cake was black, had the usual crystalline appearance of pure fused $UF_4$, and showed vitreous fracture surfaces. Samples of the salt and of the metal are being analyzed.

## B. RESULTS OF PREVIOUS OXIDE DROSSING EXPERIMENT

The fission product analyses of an oxide drossing experiment carried out during the previous quarter have been partially completed and the results are shown in Table I.

TABLE I

FISSION PRODUCTS REMOVED BY OXIDE DROSSING

| Fission Product | Amount Removed (%) |
|---|---|
| Cesium | 98.1 |
| Cerium | 97.9 |
| Tellurium | 94.9 |
| Rare Earths | 99.7 |
| Strontium | 99.8 |
| Ruthenium | 1.0 |

## C. MOLD DISASSEMBLY AND SLUG CROPPING (J. Guon)

### 1. Oxide Drossing Experiment

Molds used in an oxide drossing experiment were disassembled and the components were checked for radioactivity. The survey was made approximately three weeks after casting, using a Juno radiation detector. Most of the activity was concentrated in the skull and at the top of the riser.

The shape of the skull was similar to that of the original slugs; this crust was less than 0.010 inches thick and moderately flexible.

### 2. Slug Cropping

An experiment was carried out to study cold-short cropping of irradiated uranium and to determine the degree of contamination of equipment resulting from this type of operation.

Six irradiated slugs were cold-short cropped. It was intended that one section from each slug be approximately 4-3/4 inches long after stripping, Fig. 1. A fifteen-ton punch press was used to deliver the impact load.

Because of the weight of the punch press, a special cart was constructed, Fig. 2. Four casters were used as wheels and four truck locks were modified to support the cart weight when in position. The table was made from 3/4-inch plywood and was covered with 1/16-inch aluminum. Aluminum angles supported the top aluminum plate and the top isolation box was sealed to the plate. A polyvinyl bag was fabricated to fit inside the frame and was attached by flaps which were welded to the bag. The bag overlapped the hole in the top plate sufficiently to allow sealing after the run had been completed. A plexiglass door was fabricated opposite the transfer door. Air was exhausted from the end opposite the door by a filter box, Fig. 3. This box contained a fiberglass filter and a blower. Inside the cart was a freezer chest and lid, and a set of manipulator clips, Fig. 4.

One slug at a time was received in a polyvinyl bag. The slug was transferred to the freeze chest and the bag was cut and discarded. After all six slugs were in the chest, liquid nitrogen was added and the slugs were cooled for four hours. After all slugs had been fractured and allowed to warm to room temperature, the segments were transferred to storage.

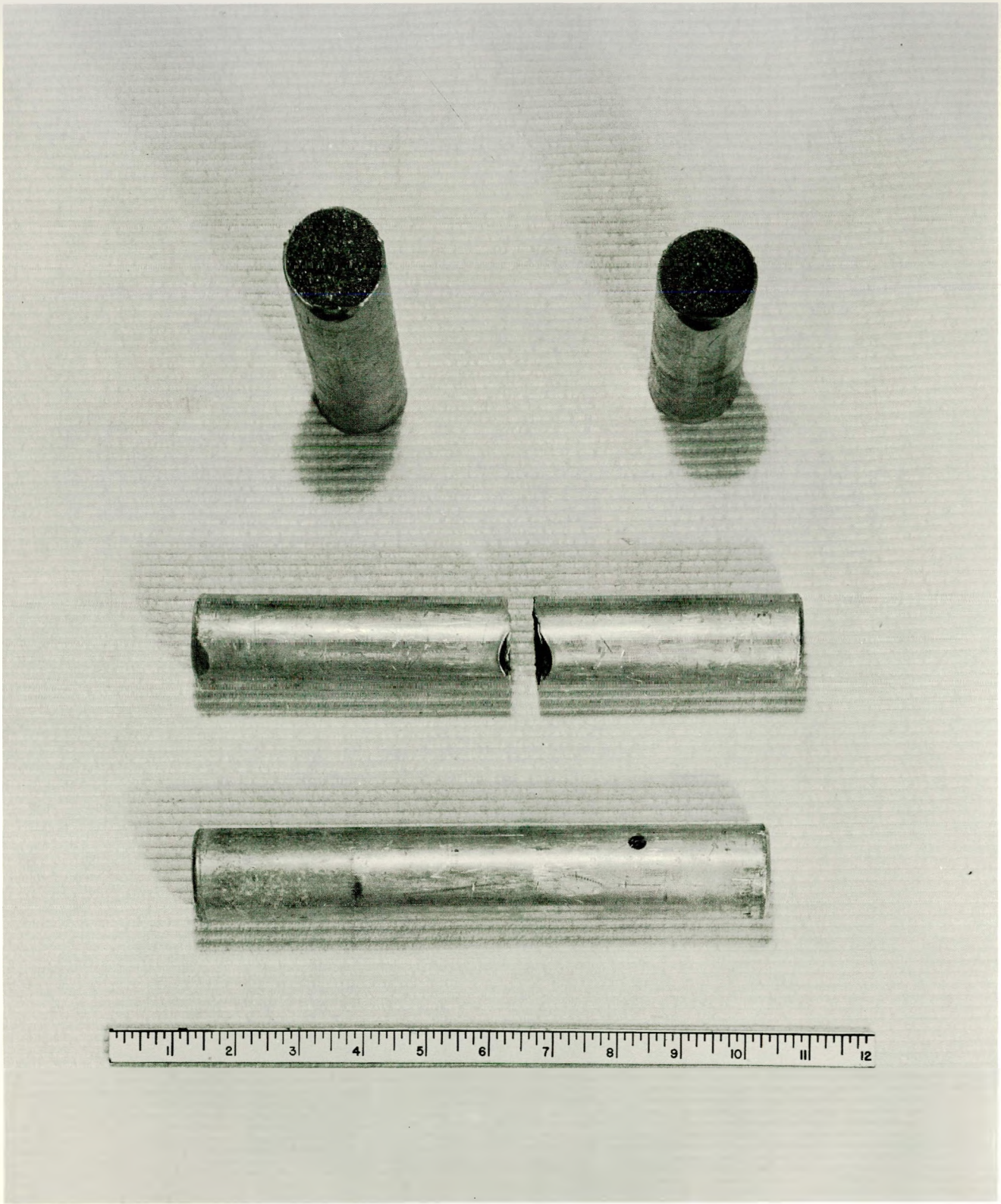



Fig. 1. Cold-short Cropped Slugs

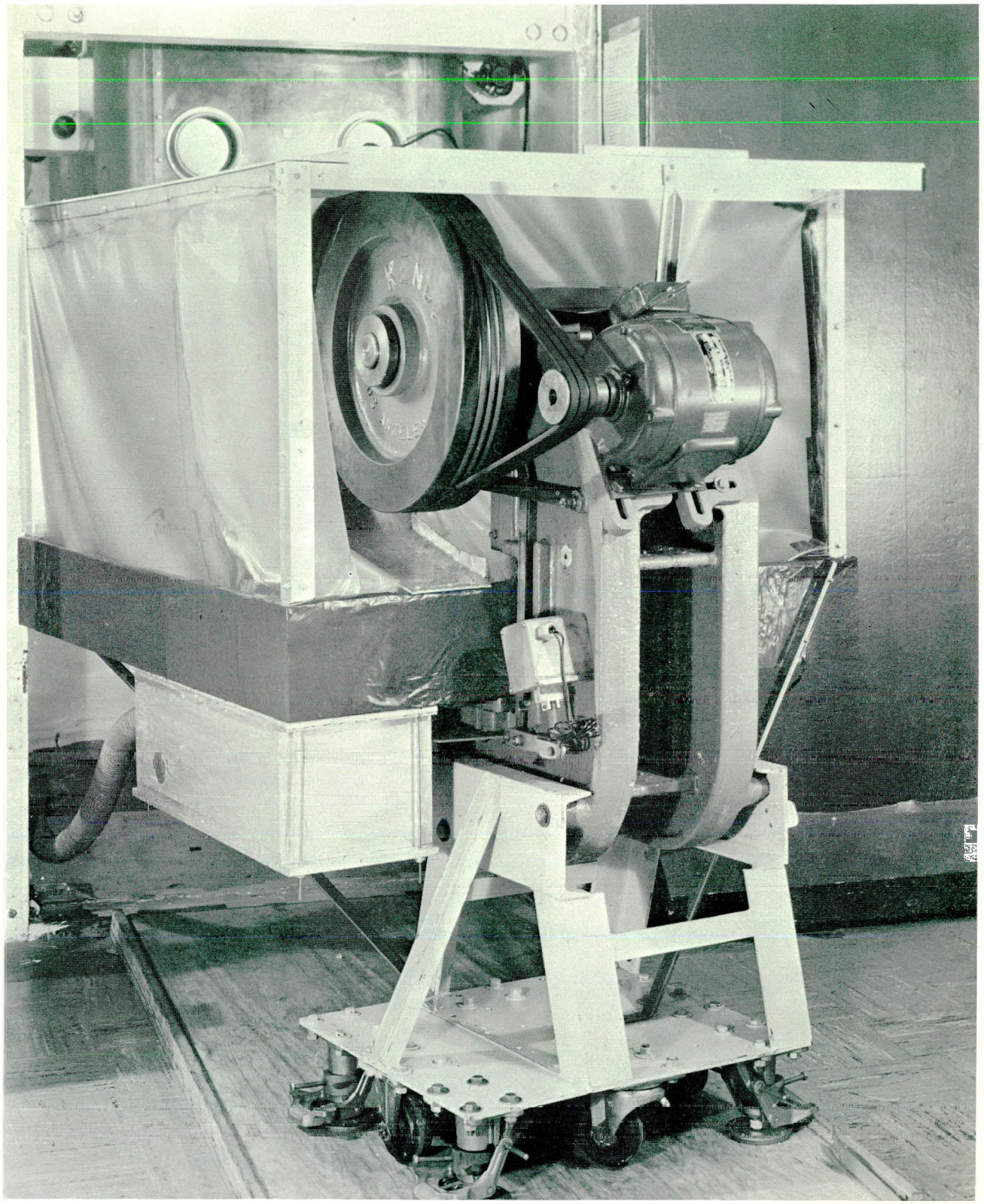


Fig. 2. Cropping Cart

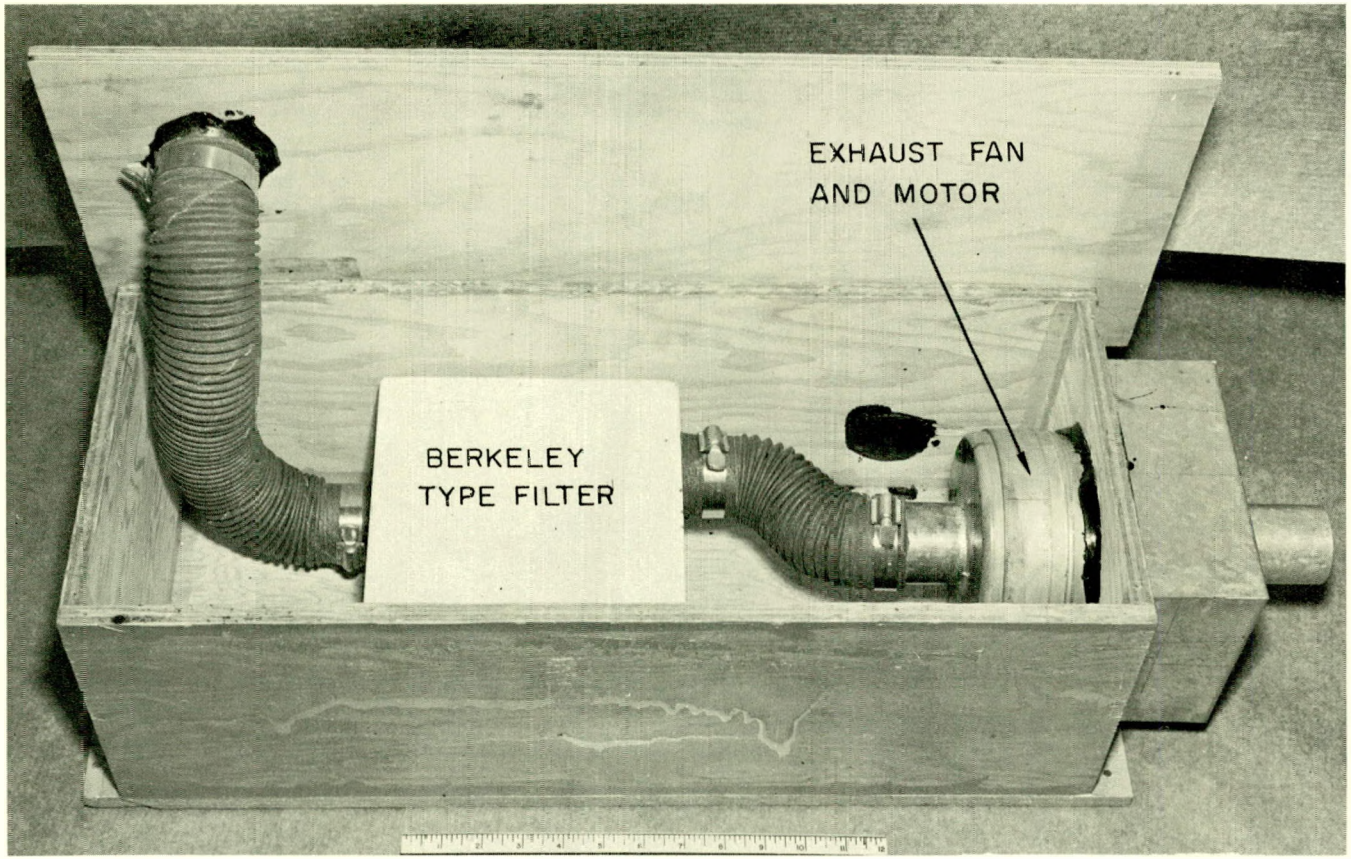



Fig. 3. Filter Box

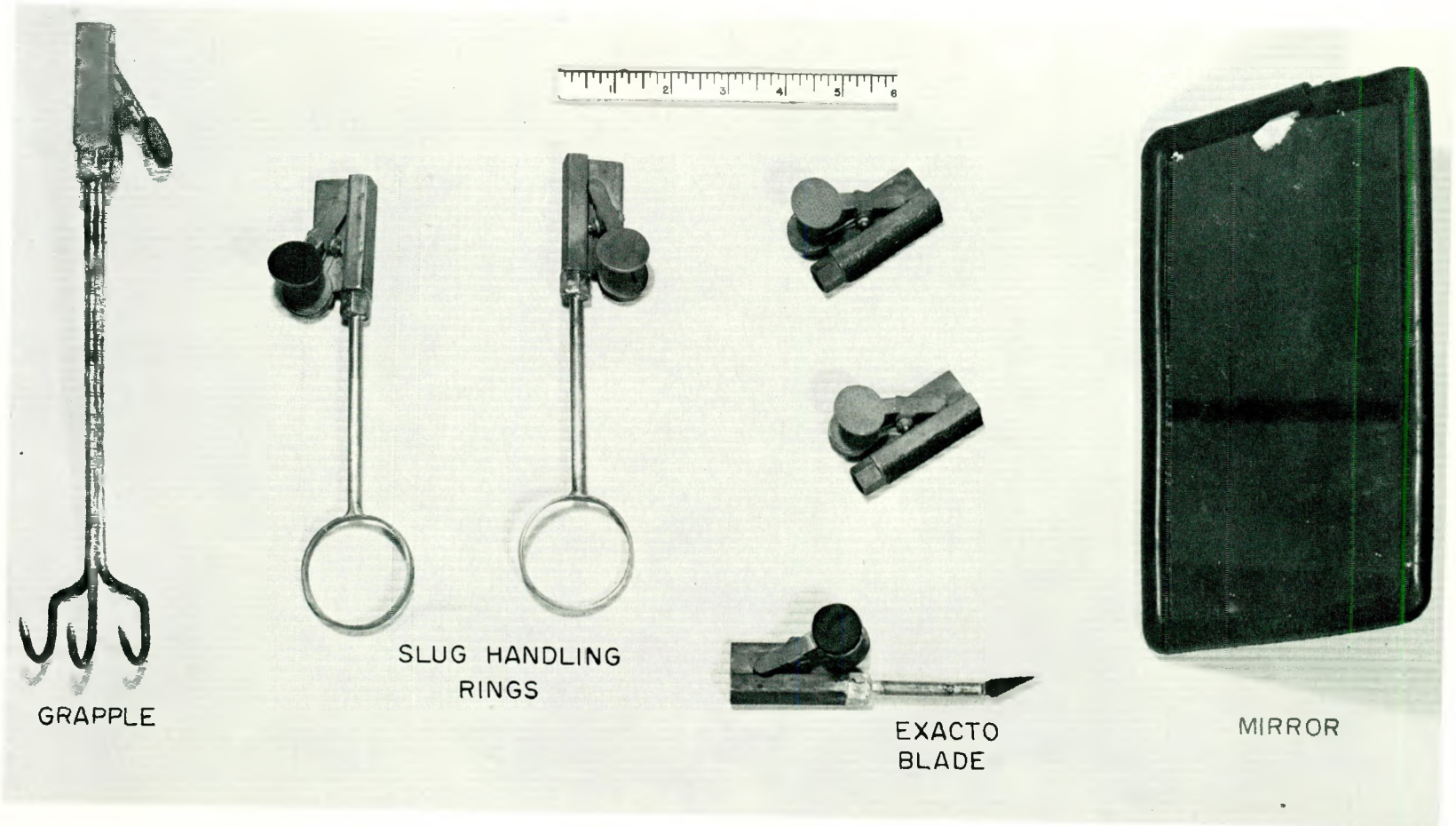



Fig. 4. Manipulator Finger Tools

The level of activity within the cell, after all segments had been transferred, was 17 mr/hr, measured at the center. Several 1-r/hr sources, located in the vicinity of the press, proved to be chips of uranium. These chips were removed on a piece of adhesive tape. All remaining sources measured less than 3 mr/hr. The sources are broken down in Table II. No component came in direct contact with uranium because the aluminum jackets had been left intact.

TABLE II

RADIATION SOURCE BREAKDOWN

| Item | Radiation* | |
|---|---|---|
| | "Jordan Meter" measurement (mr/hr) | "Classmaster" measurement (disintegrations/min) |
| Manipulators | 17-18 | - |
| Knife | 17 | 350.00 |
| Ring | 17 | 600-1400 |
| Hook | 17 | 500 |
| Sandpaper finger, 2 ea. | 17 | 5000-15,000 |
| Mirror | 18 | - |
| **"V" blocks, 2 ea. | - | 10,000-15,000 |
| Freezing chest | 20 | - |
| Shim | - | Background |
| Tup | - | Background |
| **Tup striking edge | - | 9000 |

*Background radiation was 17 mr/hr and 100 disintegrations/min.

**These parts were involved directly in the fracture; no attempt was made to remove any contamination.

## III. MECHANISM OF FISSION PRODUCT EXTRACTION–OXIDE DROSSING
(T. Smith)

The determination of the mechanism by which fission products are extracted from uranium by oxide drossing has been undertaken. The initial phase of this study was the determination of the rate of diffusion of a representative fission product, cerium, in molten uranium. The first step in this study was the determination of the solubility of cerium in molten uranium.

The solubility of cerium in uranium was determined in the temperature range 1135-1450° C. This determination permitted the ratio $C/C_s$ to be determined accurately, and from this information diffusion coefficients were calculated. In this ratio, C is the concentration of cerium at some distance x from the cerium-uranium interface into the uranium; and $C_s$ is the concentration of cerium in the uranium at the interface. $C_s$ is assumed to be the solubility of cerium in uranium at the temperature of the experiment.

The results of experiments made to find the solubility of cerium in uranium are shown in Table III. It is seen that experiments 1A, B, C, and D gave erratic results and reasonably large average error. The remaining data prove fairly consistent and have a much lower error. Table IV gives the results of White[1] for comparison. If one uses a value of $C_s$ = 2 per cent rather than 1 per cent, as used in the last quarterly report, the diffusion coefficient, evaluated from the portion of the per cent cerium vs x curve that is least sensitive to $C_s$, is decreased by about 30 per cent.

A new furnace system was designed and constructed and is illustrated in Fig. 5 and 6. The purpose of the apparatus is to provide a system in which the rate of extraction of fission products from uranium can be measured. In particular, the system has been built so that the molten uranium can be stirred with the oxide body during the extraction and samples of molten uranium can be taken with a quartz tube.

Two preliminary oxide drossing experiments have been made using MgO and $ZrO_2$ solid cylinders. Tables V and VI give the experimental conditions and the available results. These were exploratory experiments and stirring was not used.

TABLE III

SOLUBILITY OF CERIUM IN URANIUM

| Experiment No. | Temp. (°C) | Ce in U (w/o) | No. of Samples Averaged | Average Error | Crucible Material |
|---|---|---|---|---|---|
| 1A | 1140 | 1.80 | 3 | 0.28 | Ta |
| 1B | 1140 | 0.70 | 1 | - | Ta |
| 1C | 1315 | 0.93 | 3 | 0.21 | Ta |
| 1D | 1315 | 0.91 | 7 | 0.41 | Ta |
| 12 | 1350 | 1.91 | 3 | 0.22 | W |
| 11 | 1480 | 1.80 | 1 | - | Ta |
| 15A | 1345 | 2.00 | 2 | 0.11 | Ta |
| 15B | 1345 | 2.03 | 2 | 0.03 | Ta |
| 15C | 1345 | 2.11 | 2 | 0.05 | Ta |
| 15D | 1345 | 2.09 | 2 | 0.01 | Ta |

TABLE IV

SOLUBILITY OF CERIUM IN URANIUM BY WHITE[1]

| Temp. of Quench (°C) | Ce in U (w/o) | U in Ce (w/o) |
|---|---|---|
| 1137 | 1.17 | 3.48 |
| 1170 | 1.30 | 3.10 |
| 1200 | 1.16 | 3.70 |
| 1228 | 1.44 | - |

TABLE V

PRELIMINARY OXIDE DROSSING EXPERIMENT NO. 14

EXPERIMENTAL CONDITIONS:

| | | |
|---|---|---|
| U-Ce Alloy | = | 0.5% Ce, 76 gm |
| Crucible | = | W, 1.7 cm diam x 4 cm deep |
| Oxide Solid Cylinder | = | MgO, 1 cm diam x 5 cm long; 3 cm contacted the U-Ce alloy |
| Temp. | = | 1235° C |
| Time of Contact | = | 90 min |
| Area Weight | = | 0.134 $cm^2$/gm |

RESULTS:

| Sample No. | Portion in Uranium Slug Used | Ce in U (w/o) | Amount of Ce Removed (%) |
|---|---|---|---|
| 1c | Top center | 0.09 | 82 |
| 2c | Middle center | 0.02 | 96 |
| 3c | Middle center | 0.01 | 98 |
| 4c | Bottom center | 0.01 | 98 |
| 1 | Top outside | 0.03 | 94 |
| 2 | Middle outside | 0.03 | 94 |
| 3 | Middle outside | 0.10 | 80 |
| 4 | Bottom outside | 0.01 | 98 |

Note: Samples from the MgO body are still being analyzed.

TABLE VI

PRELIMINARY OXIDE DROSSING EXPERIMENT NO. 16

EXPERIMENTAL CONDITIONS:

| | | |
|---|---|---|
| U-Ce Alloy | = | 0.5% Ce, 123 gm |
| Crucible | = | Ta, 1.8 cm diam x 4 cm deep |
| Oxide Solid Cylinder | = | $ZrO_2$, 1 cm diam x 5 cm long; 3 cm contacted the U-Ce alloy |
| Temp. | = | 1220° C |
| Time of Contact | = | 55 min |
| Area Weight | = | 0.0083 $cm^2/gm$ |
| Atmosphere | = | Argon |

Note: Samples of molten U were taken with 3 mm quartz tube

RESULTS:

| Sample No. | Time After Contact (min) | Portion of Material Used | Ce in U (w/o) | Amount of Ce Removed (%) |
|---|---|---|---|---|
| 1' | 13 | Center to one side of oxide body | - | - |
| 2' | 27 | Center to one side of oxide body | 0.06 | 88 |
| 3' | 45 | Center to one side of oxide body | 0.02 | 96 |
| 4' | 65 | Center to one side of oxide body | 0.03 | 94 |
| 1c | 90 | Top center of U slug | 0.12 | 76 |
| 2c | 90 | Bottom center of U slug | 0.09 | 82 |
| 1 | 90 | Top outside of U slug | 0.06 | 88 |
| 2 | 90 | Bottom outside of U slug | 0.05 | 90 |
| 7 | 90 | U that clung to the oxide body | 0.39 | 22 |

Note: The primed samples were taken while the U was molten, the others were taken on the lathe after cooling.

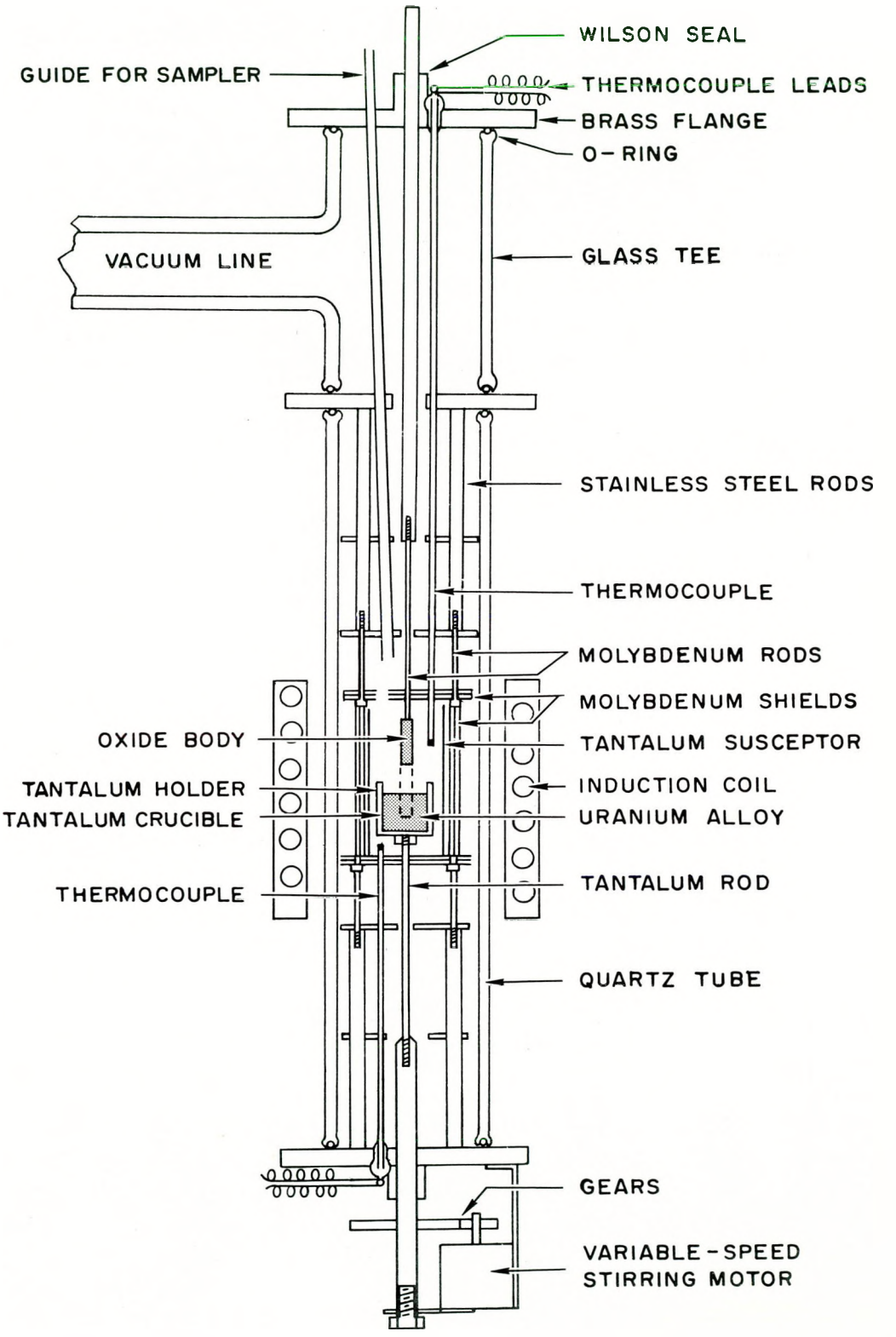



Fig. 5. Schematic of Oxide Drossing Vacuum Furnace

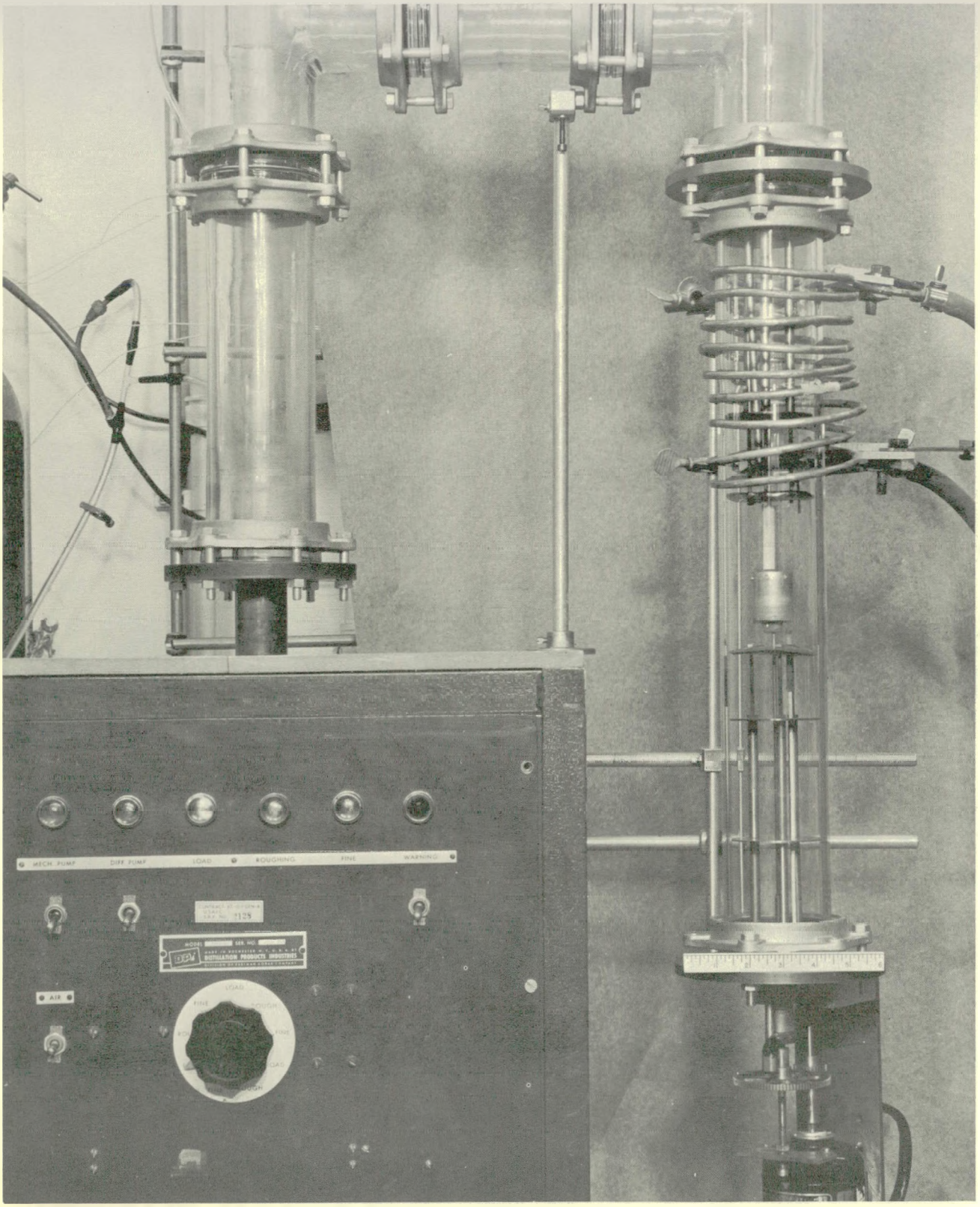



Fig. 6. Oxide Drossing Vacuum Furnace

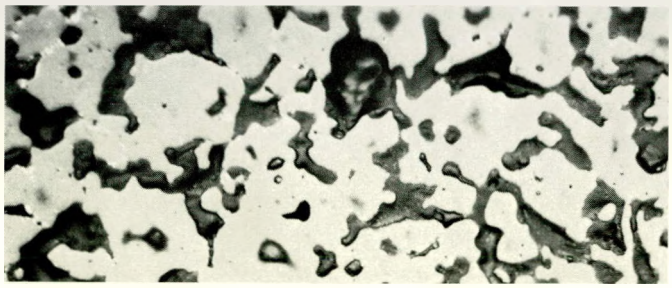
During these experiments the reaction was so fast that the effect of time could not be measured. In subsequent experiments the system will be adjusted so that the effect of time, stirring, and temperature can be determined. During experiment No. 14, in which MgO was used, the cylinder was removed from the molten uranium without adhering. A brown film, about 0.005-inch thick, formed on the oxide cylinder and peeled off very easily. This film plus two other layers of oxide which were cut from the cylinder will be analyzed for cerium and uranium. The MgO was white on the inside (as it was before the experiment).

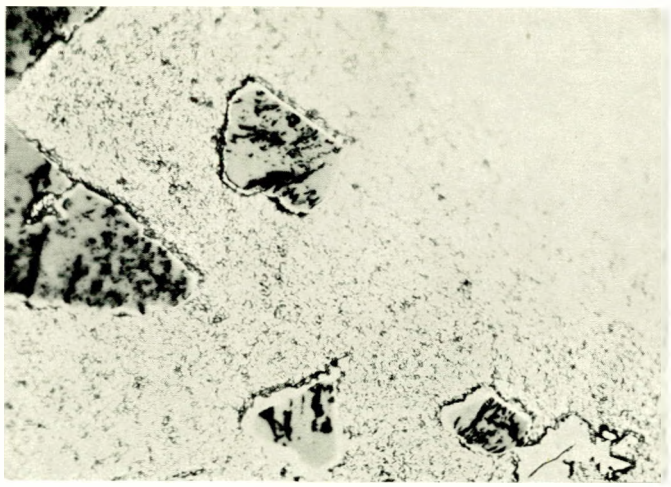
During experiment No. 16, a layer of uranium adhered to the $ZrO_2$ body when it was removed. The bottom portion of the $ZrO_2$ cylinder plus uranium was cut off to show a cross section. The stabilized zirconia had changed from yellow to black throughout the entire cylinder. The oxide is being analyzed for cerium and uranium.

The lower photograph in Fig. 7 shows a portion of the $ZrO_2$-U interface, the magnification being 100. The upper part is uranium and the lower part is $ZrO_2$. The large number of crystallites moving into the uranium from the interface are probably $UO_2$ because a sample including these crystallites dissolved readily in aqua regia; $ZrO_2$ and $Ce_2O_3$ would not. The boundary is smooth and does not appear as though $ZrO_2$ broke off to form these crystallites. The crystallites were gray as compared to the much lighter $ZrO_2$ phase. Three or four times as much of these crystallites are produced than is possible from all of the cerium present.

The center photograph in Fig. 7 shows some of the crystallite inclusions in the uranium phase; the magnification is 500. Three phases are observed: uranium, large crystallites of $UO_2$, and a white phase that surrounds the $UO_2$ crystallites.

It is thought that the white phase is $CeO_2$, the product of the reaction between the cerium and $UO_2$. The upper photograph in Fig. 7 shows the $ZrO_2$ phase at a magnification of 500; the white phase can be detected in the upper left corner. It was observed that there was very little of this white phase around the $UO_2$ crystallites near the interface, and that the amount of this white phase increased with the distance from the boundary. This suggests that the crystallites near the boundary, being newly formed, have not had time to react while those farther out have.





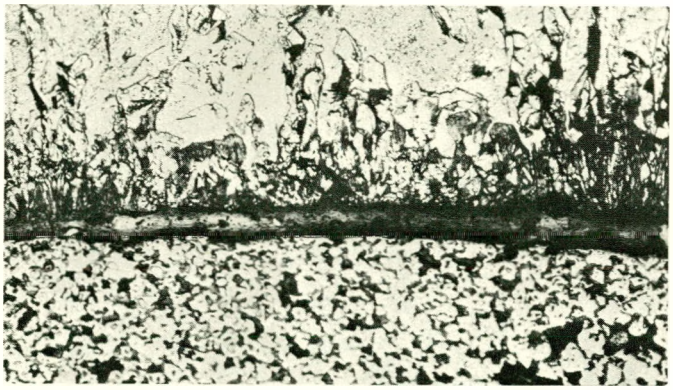


Fig. 7. Photomicrographs of $ZrO_2$ and Uranium Phases After Extraction of Cerium

It should be noted that both the $ZrO_2$ and MgO bodies were very porous, the densities being respectively 71 per cent and 73 per cent of theoretical. All of the photomicrographs were made after the specimen was polished and etched in 50 cu cm $CrO_3$ in $H_2O$ plus 12 cu cm $CH_3$ COOH.

From these experiments it was learned that:

1) The experimental technique will probably work.
2) A much smaller area weight ratio is needed to measure the extraction rate.
3) The cerium has concentrated as the reaction product in the uranium near the oxide body; see samples 7 and 1c, Table VI.

## IV. HIGH TEMPERATURE SEPARATIONS CHEMISTRY OF THORIUM FUELS

High temperature separations chemical studies concerning thorium fuels have been directed toward the removal of fission products by means of the following processes: evaporation from fuels melted under vacuum, extraction by contact with liquid zinc, electrorefining in molten halide baths, and gravity flow through calcium fluoride beds.

### A. EVAPORATION FROM VACUUM-MELTED FUELS (W. Murbach)

Two approaches have been applied to the investigation of fission product evaporation from vacuum-melted thorium fuel. These were "nonconsumable arc melting" and "drip melting". The latter is carried out by suspending an irradiated fuel rod within a high-frequency induction field, maintained in a vacuum.

The suspended metal melts at the field focal point, drips off, and drops into a copper mold.

#### 1. Arc Melting of Thorium-Uranium

The analyses on Series 5 experiments, conducted during the previous quarter, were completed. The results are presented in Table VII.

These data are quite similar to those obtained previously. The results show that high uranium and protactinium losses result from excessive heating.

TABLE VII

EVAPORATION LOSS BY ARC MELTING OF IRRADIATED Th-3 w/o U ALLOY

| Experiment No. | Time (min) | Weight (gm) | Temp. (°C) | Element and Amount Removed (%) | | |
|---|---|---|---|---|---|---|
| | | | | Pa | U | Th |
| 23 | 5 | 2.36 | 1900 | 24.2 | 3.53 | 0.68 |
| 24 | 20 | 2.99 | 1900 | 36.7 | 17.3 | 3.16 |
| 25 | 10 | 3.97 | 2000 | 29.2 | 10.45 | 3.04 |
| 26 | 5 | 4.11 | 2100 | - | 13.63 | 2.43 |
| 27 | 30 | 4.82 | 1800 | - | 0.74 | 0.70 |

Examination of some of the results from removals of protactinium, thorium, and uranium indicates that an estimate could be made of the vapor pressures of thorium and protactinium. The vapor pressures of these elements, according to the literature, are only estimated; therefore, a series of calculations were made on the basis of experimental data obtained in this work.

The assumption was made that these elements form ideal solutions with uranium. If valid, the amounts volatilized would be in direct proportion to the vapor pressures of the elements. For lack of exact data, the heats of vaporization of protactinium and thorium were assumed to be equal to that for uranium. The value for the vapor pressure of uranium was taken from the work of Rauh and Thorn.[2]

Using these assumptions, the vapor pressure equations derived for thorium and protactinium are:

Thorium; $$\log P_{(atm)} = \frac{-2.33 \times 10^4}{T} + 5.15$$

Protactinium; $$\log P_{(atm)} = \frac{-2.33 \times 10^4}{T} + 6.33$$

The vapor pressures as calculated from these experiments are somewhat higher than the estimates.

The laboratory-scale consumable arc melting furnace has been completed and preliminary tests were made. A photograph of the furnace appears in Fig. 8.

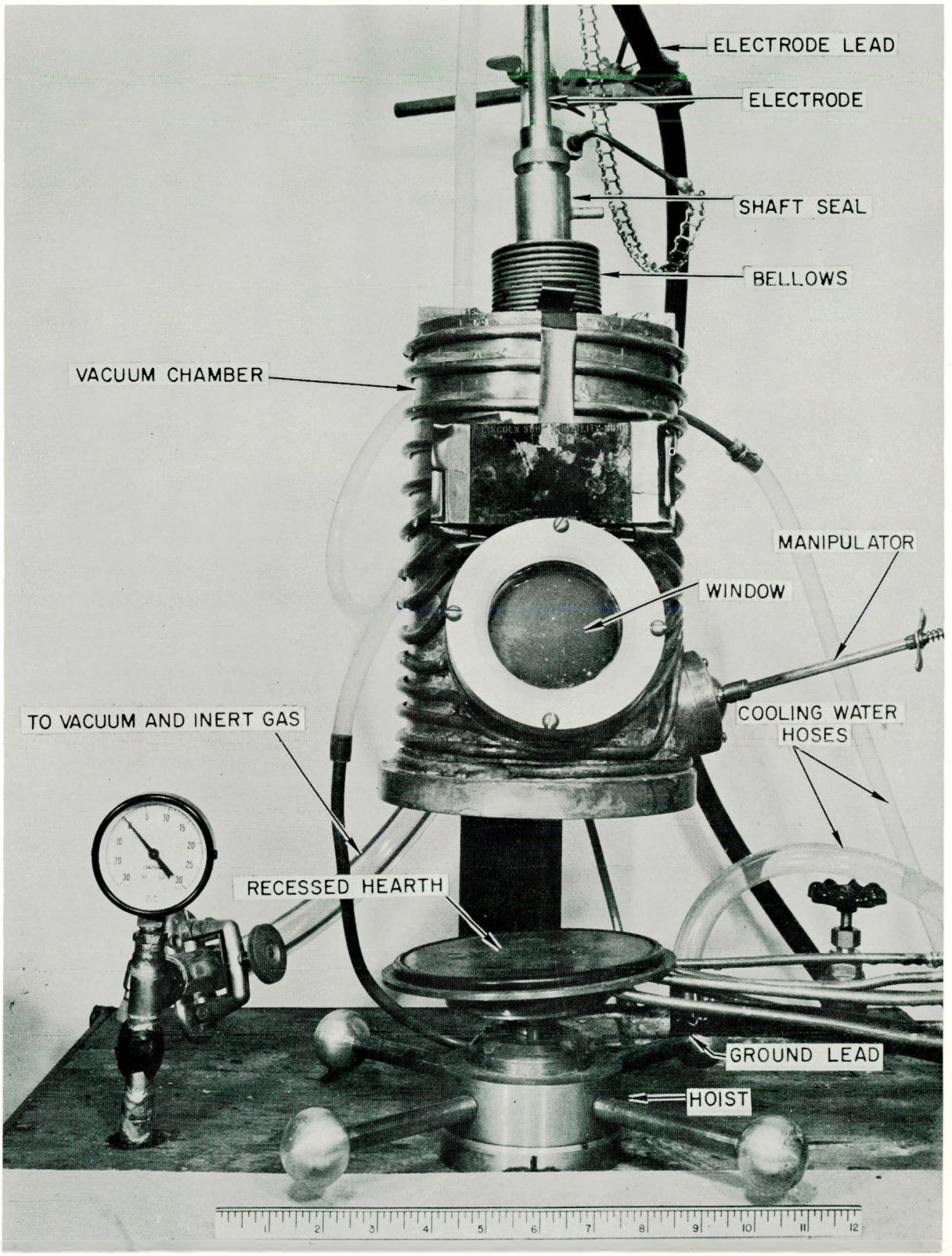



Fig. 8. Consumable-arc Furnace

The electrode holder cannot be seen, but it consists of a recessed copper block, silver soldered to the end of the water-cooled electrode. The piece to be melted is held in the copper block by set screws. During melting, the molten metal flows into the large recess in the water-cooled copper hearth.

Accessories for the furnace include the power supply, a Model 302 P & H direct current welder, and a mechanical vacuum pump for inert gas flushing of the furnace. The hoist for elevating the hearth to the closed position is hand operated.

The electrode is insulated by a teflon ring which is located between the bellows and the top of the furnace. This assembly is sealed to the system by high melting wax. The system can be readily evacuated to 25 microns which is the limit of the mechanical pump currently in use.

The furnace has also been used as a nonconsumable arc melter by substituting a solid tungsten tip in place of thorium in the electrode holder. The manipulator is used for inverting samples melted in this manner; thus, this is an extremely versatile laboratory tool.

To date, several pieces of thorium-uranium alloy weighing up to 100 grams have been satisfactorily melted by the consumable arc melting technique. Decontamination experiments on irradiated thorium-uranium alloy by consumable arc melting are planned for the near future.

2. Drip Melting

An alternate process for the decontamination of thorium-uranium alloy by direct volatilization of fission products is currently being studied. Briefly, the process consists of melting a fuel slug while suspended in high-vacuum, high-frequency induction field.

Melting by this method obviates the contamination problem which occurs when melting is done in a crucible. At the melting point of thorium many of the fission products are quite volatile.[3] If thin films can be melted from the sample, decontamination from a number of fission products would be expected.

A "drip melting" process has previously been used[4] for melting zirconium alloys.

Figure 9 is a photograph of the apparatus now being used. The vacuum tube is a 51-mm diameter Vycor tubing. The piece to be melted is suspended on a tantalum rod in the apparatus. The water-cooled induction coil is powered by a 6 kw Ajax convertor. A copper mold is placed in the bottom of the tube to catch the molten metal. The furnace tube is waxed into a brass flange which is sealed to the high vacuum system by an O-ring seal. The system is evacuated by an oil-diffusion pump and a mechanical fore pump.

The first experiment was conducted with a rod of Th-10 w/o U alloy approximately 1/4 inch square and 3 inches long. Figure 10 is a photograph of the resulting product. As can be seen, most of the drops were not strongly bonded and were easily broken apart. The manner in which the drops formed from the remainder of the rod is shown in Fig. 10. It was interesting to note that the rod was very bright after removal from the vacuum system. Also, the inside of the vacuum tube was heavily blackened, undoubtably from some impurity in the alloy which volatilized.

To date, only a few experiments to check out equipment and melting technique have been carried out. The 6 kw Ajax convertor is actually too small for this method, because alloys which melt at higher temperatures than Th-10 w/o U could not be melted. However, various modifications of furnace tubes, coils, and induction heaters are being investigated. Decontamination experiments on irradiated material are planned for the near future.

## B. EXTRACTION OF FISSION PRODUCTS WITH MOLTEN ZINC (F. W. Dodge and W. N. Hansen)

The zinc extraction procedure described below was initiated during this period. The method consists of: dissolving thorium metal or alloy in molten zinc to near saturation, at close to the boiling point of zinc; filtration at this temperature to remove oxides and other insoluble material; cooling of the filtrate to near the melting point of zinc; and of a second filtration to remove precipitated solids, chiefly thorium-zinc or thorium-uranium-zinc compounds. Available data indicate that the fission products, present in small quantity in the irradiated fuel, are sufficiently soluble in zinc near its melting point to remain largely in the filtrate, thus effecting decontamination. Thorium and uranium are separated from the zinc by vacuum distillation.

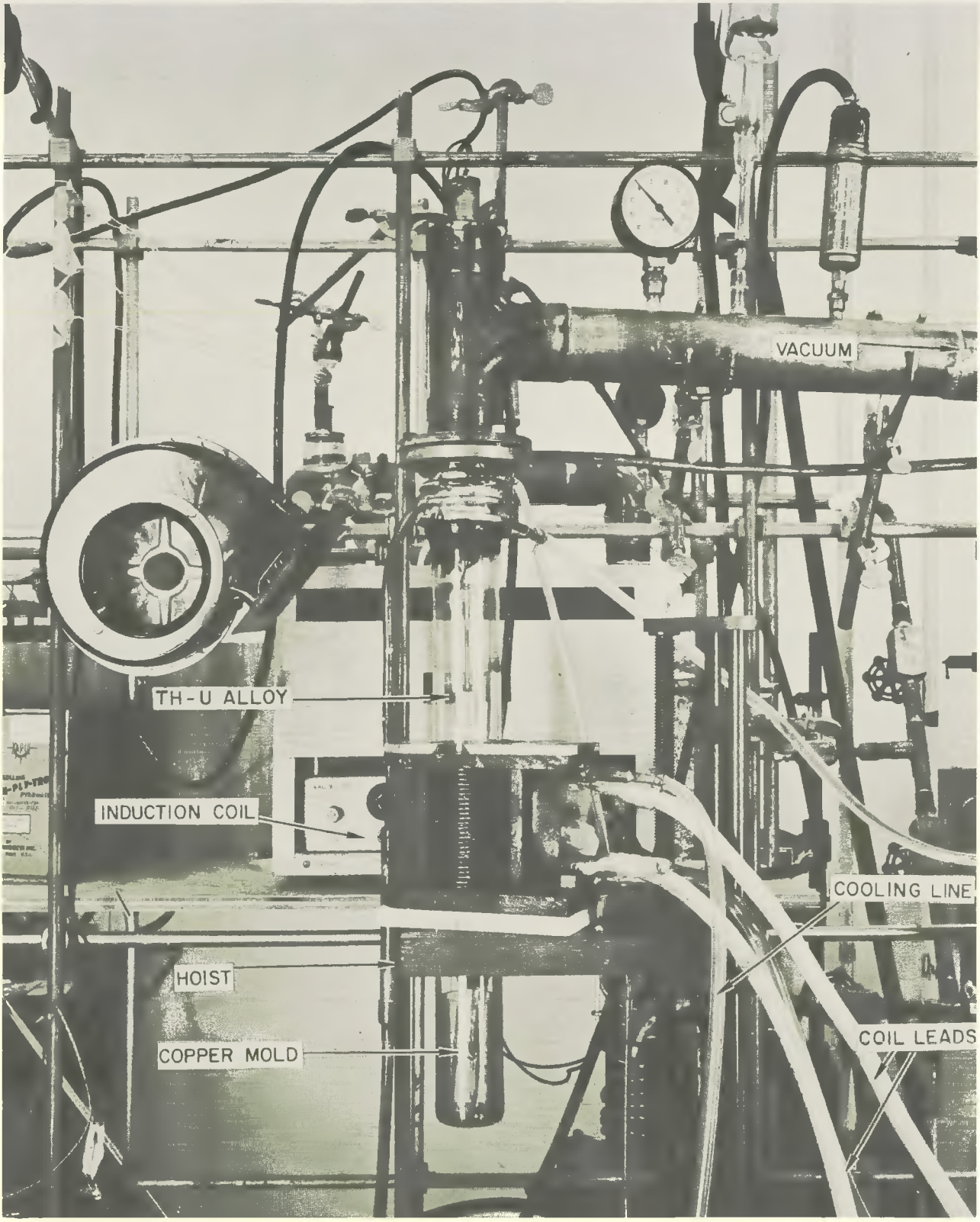



Fig. 9. Drip-melting Apparatus


Fig. 10. Drip-melted Thorium-uranium Alloy

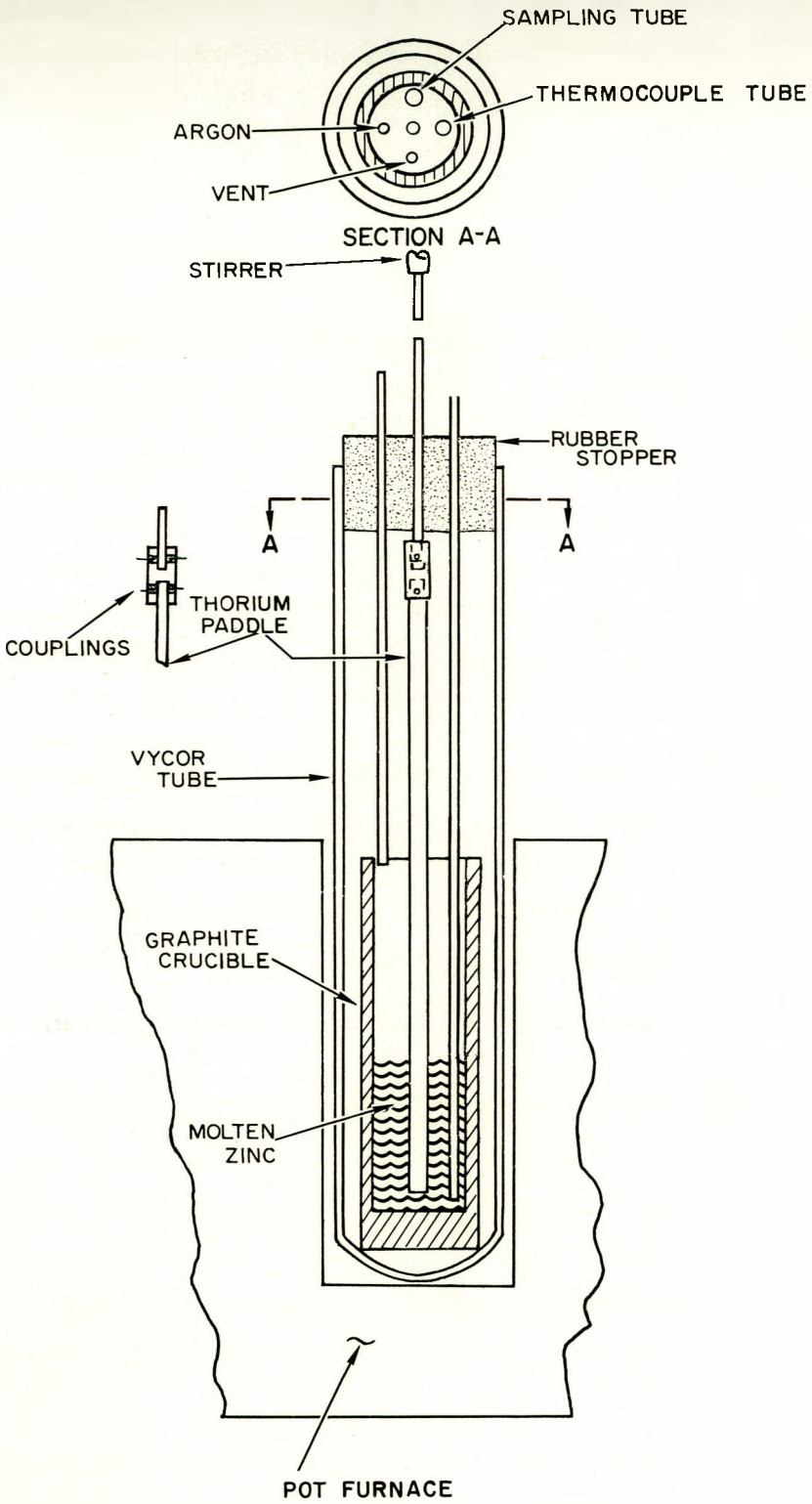



Fig. 11. Thorium-zinc Dissolver

Preliminary work using this approach has been promising, and has already indicated several advantages: 1) Since the maximum temperature involved is the boiling point of zinc, 917° C, the problem of materials of construction is considerably reduced; graphite crucibles have been found to be satisfactory; and Vycor is resistant to molten zinc and zinc vapor. 2) A thorium "paddle" slowly rotated in molten zinc dissolves rapidly up to about 8 per cent, i.e., 28 grams of thorium in 300 grams of zinc in 45 to 60 minutes. 3) On cooling, precipitated thorium-zinc crystals tend to settle rapidly, indicating good crystal growth, which should facilitate filtering. 4) Perhaps the most important advantage, as indicated by data available to date, is that no thorium-zinc eutectic is formed in the range studied and the solubility of thorium in zinc is conservatively less than 0.1 w/o at the freezing point of zinc. Thus, with close temperature control, it may be possible to hold the loss of thorium in the zinc phase low enough to preclude the necessity for reclaiming thorium from the zinc, and the zinc may be recycled without further loss of thorium until the concentration of fission products approaches saturation.

A sketch of a laboratory apparatus which has proved satisfactory for dissolving thorium in molten zinc is shown in Fig. 11. Liquid samples are obtained by introducing a quartz or Vycor tube into the liquid through the normally stoppered sampling tube. Dissolution of thorium is estimated by lowering the paddle until it touches the crucible bottom and measuring the change in length.

Using the apparatus shown in Fig. 11, the solubility of thorium in zinc was determined at various temperatures by the following technique. The temperature of the zinc was raised nearly to its boiling point and thorium was added until dissolution of the thorium paddle became so slow as to be visually imperceptible and the temperature remained constant. The paddle was removed and a sample was taken from just below the surface of the melt. The temperature was lowered and held constant for about twenty minutes at some desired value. A sample was then taken at this temperature. In the same manner samples were obtained at various temperatures.

Previous experimentation had shown that the crystals form and sink rapidly as the molten alloy is cooled. The sampling method used would therefore seem to be valid. Reproducibility of data would establish this point.

Table VIII contains the data obtained thus far. These data are given in graphical form in Fig. 12.

TABLE VIII

SOLUBILITY OF THORIUM IN ZINC

| Temp. °C | Per Cent Th |
|---|---|
| 881 | 8.38 |
| 755 | 3.00 |
| 600 | 1.18 |
| 518 | 0.49 |

C. ELECTROREFINING OF Th-U ALLOY (W. N. Hansen)

A sample of Th-10 w/o U alloy which had been irradiated to a low level of activity was electrolyzed. The starting salt bath constituent mole ratios were 1:1:0.1 for NaCl, KCl, and $ZnCl_2$ respectively. The salt was contained in a graphite crucible, and a recrystallized alumina crucible containing zinc was immersed in the molten salt. The thorium-uranium alloy was placed in the bottom of the graphite crucible and served as the anode. The zinc pool served as the cathode. After the electrolysis stopped and before the salt cooled, the crucible containing the cathode was removed from the salt bath.

Using the above procedure, preliminary decontamination was obtained in the percentages indicated in Table IX. The uranium was found to follow the thorium in the electrolysis.

TABLE IX

Th-10 w/o U DECONTAMINATION RESULTS

| Element | Amount Removed (%) |
|---|---|
| Zirconium | 58 |
| Cerium | 79 |
| Rare Earths | 84 |
| Ruthenium | 91 |
| Strontium | 99 |
| Cesium | 99 |

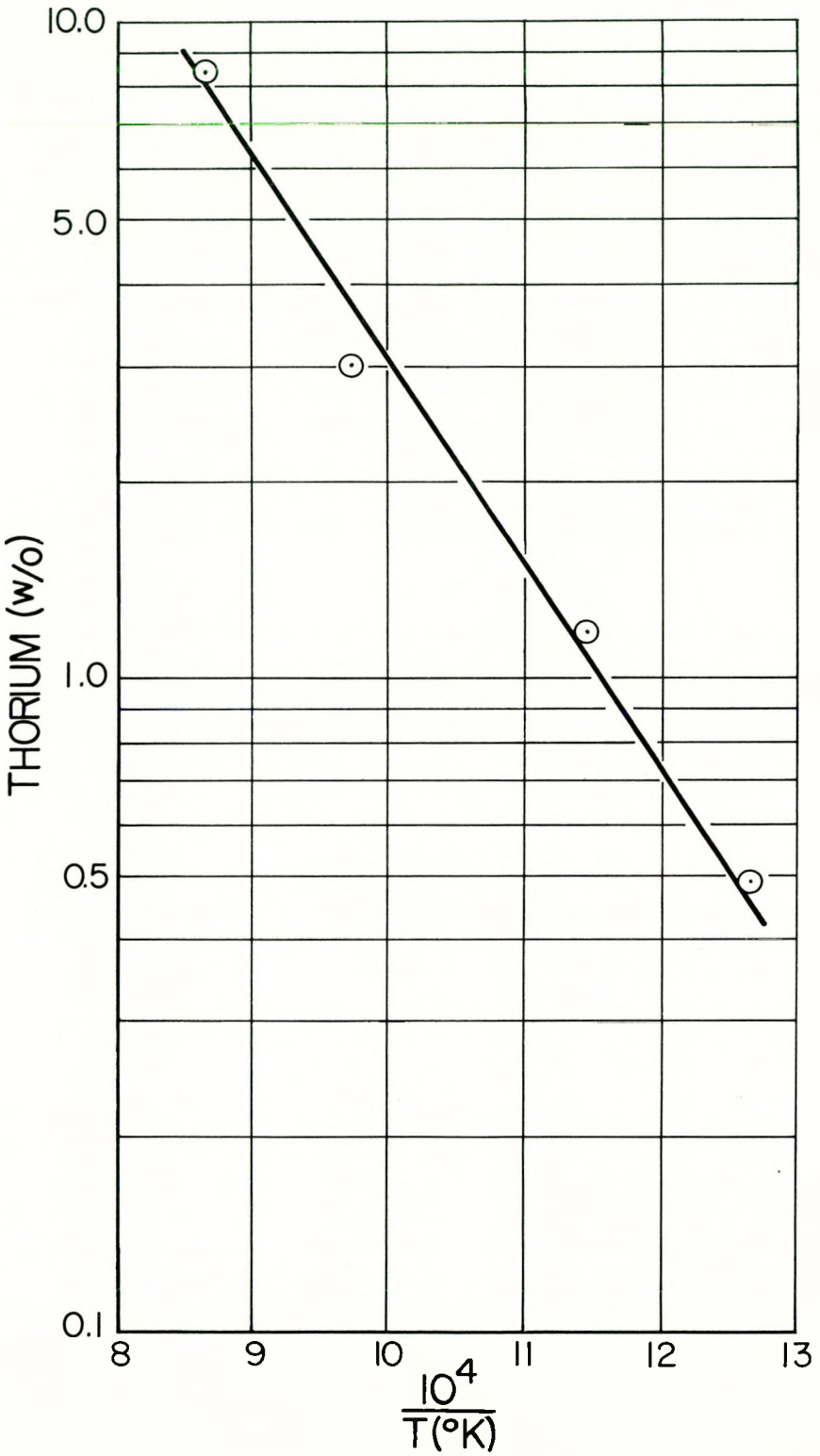



Fig. 12. Solubility of Thorium in Zinc

An electrolysis run was made using "cold" Th-10 w/o Zr alloy as anode material and a salt bath composition as above. It was found that zirconium at these concentrations followed the thorium into the zinc and during the first part of the electrolysis the zirconium was transported to the cathode more rapidly than the thorium. This observation is not surprising in view of the data calculated for the free energy of formation of zirconium and thorium chlorides.

### D. GRAVITY FLOW THROUGH FROZEN CALCIUM FLUORIDE BEDS
(A. G. Buyers and J. Chilton)

Thorium-uranium (10 w/o) alloy samples have been partially decontaminated using a salt-bed process. The method consists of induction melting the alloy supported by a vertical column of compacted calcium fluoride. The molten metal then melts its salt environment and, under gravity, passes down through the salt column.

Experiments in which melting periods of from 3 to 28 minutes for the irradiated metal, and calcium fluoride columns of from 1 to 6-1/8 inches in length were used have disclosed removal of 35 to 98 per cent cerium, strontium, rare earths, and cesium. Seventy to 80 per cent tellurium was removed. Thorium losses amounted to 1 to 12 per cent. Zirconium, ruthenium, protactinium, and uranium were not appreciably extracted by the salt bed.

It is suggested that this salt-metal system does not reach equilibrium with regard to fission product and fissionable element distribution. This entire investigation is discussed in detail in a topical report.[9]

## V. SUMMARY

An experiment was carried out to study the extraction of plutonium from molten uranium by fused uranium fluoride.

The analytical results of a previous kilogram scale oxide drossing experiment show the following fission product removals: 98 per cent cesium and cerium, 95 per cent tellurium, over 99 per cent rare earths and strontium, and 1 per cent ruthenium.

Six irradiated Hanford slugs were successfully cold-short cropped. The spread of contamination within the cell was very small.

A study of the mechanism of fission product extraction by means of oxide drossing has been undertaken. As an initial step in this investigation the solubility of molten cerium in liquid uranium has been checked and found to approximate 2 per cent rather than 1 per cent as reported by other workers. Magnesia and zirconia drossing of U-Ce alloy have been carried out indicating that the extracted cerium (oxide) concentrates in the uranium metal near the metal oxide interface.

Final decontamination data obtained by non-consumable arc melting of irradiated thorium-uranium alloys show that at extreme temperatures and heating times the evaporation loss of protactinium is from 24 to 36 per cent and the loss of uranium is from 1 to 14 per cent. This work has indicated that reported vapor pressures for thorium and protactinium are low.

Two new pieces of equipment, a consumable arc melting furnace and a vacuum induction-melting device (drip melter), have been constructed and preliminary experiments were completed.

Extraction of fission products from Th-U alloy with molten zinc has been undertaken. Apparatus has been completed and preliminary experiments have been carried out.

Electrolysis of irradiated Th-10 w/o U using molten 1:1:0.1 NaCl-KCl-$ZnCl_2$ and a liquid zinc cathode, resulted in removal of 58 per cent zirconium, 79 per cent cerium, 84 per cent rare earths, 91 per cent ruthenium, and greater than 99 per cent strontium and cesium. Both thorium and uranium were electrolyzed into the zinc cathode.

Experiments in which irradiated Th-10 w/o U was melted by induction heating and allowed to melt through frozen calcium fluoride columns have demonstrated greater than 80 per cent removal of cesium, strontium and tellurium. Ruthenium, protactinium, zirconium and uranium losses were negligible. Thorium losses to the salt bed were found to approach 12 w/o.

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The following is a list of each previous "Separations Chemistry" Quarterly Progress Report:

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