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PYROMETALLURGICAL PROCESSES FOR THORIUM-URANIUM FUEL
SEMIANNUAL PROGRESS REPORT
JANUARY-JUNE, 1956

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.

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CHEMISTRY

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PYROMETALLURGICAL PROCESSES FOR THORIUM-URANIUM FUEL
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ABSTRACT

Exploratory studies are being conducted on the pyrochemical processing of Th-U fuel. Tracer level fission product decontamination studies using the de Boer iodide process with irradiated thorium have been terminated. This process will remove Cs, Sr, Ce, rare earths, and Ru. Zirconium and Pa are not removed.

Evaporation of fission products from crucible-contained melts of irradiated Th-(3 w/o)U alloy has been investigated. Cesium, Sr, Te, Ce, and rare earths were volatilized. The three first-mentioned activities are also evaporated from heated, unmelted alloy which had been subjected to hydriding and dehydriding to increase surface area.

Volatilization of fission product activities from arc-melted thorium alloy has yielded decontamination similar to that obtained from crucible-contained melts.

Research concerning solid and liquid oxide slagging of irradiated Th-U alloy has been completed. The latest data obtained have shown removal of 76 per cent Ce and rare earths, 100 per cent Sr, smaller amounts of Te and Zr and negligible fractions of Pa and Ru.

Salt bed decontamination studies processing irradiated Th-(10 w/o)U alloy with calcium fluoride columns have demonstrated 83 to 98 per cent removal of Ce, rare earths, Y, Te, Sr and Ce. Protactinium, Zr, and Ru wer not extracted by the salt column.

A research and development study of the electrorefining of thorium from molten halide baths has been initiated.

I. INTRODUCTION

The investigation of high-temperature methods for processing thorium reactor fuels currently in progress at Atomics International is being conducted along broad exploratory lines seeking to encompass the more promising procedures for fission product removal.

Processes under investigation include: de Boer iodide refining, evaporation of fission products from crucible-contained or arc-melted alloy samples, solid and liquid refractory slagging, molten alloy — molten salt equilibration, and electrorefining in molten salt baths.

The de Boer process tracer-level studies have been completed and for the most part, reported.[1] Apparatus for experimenting with actual fuel has been constructed, but this study has been temporarily tabled until available data on other processes permits a thorough evaluation of all likely methods.

The investigation of fission product volatilization from crucible-contained melts is reported in its entirety as this study has been completed.

II. DISCUSSION AND RESULTS

High-temperature thorium separations chemistry studies include: de Boer iodide refining in which thorium and impurity iodides are formed, selectively volatilized and decomposed; volatilization of fission products from crucible-contained irradiated Th-U alloy melts; solid and liquid oxide slagging wherein the liquid slag was an equimolar solid solution of CaO in CaF_2; molten alloy — molten salt equilibration contained in frozen salt beds; and electrorefining of irradiated thorium in fused salt baths. In this last investigation, contaminated thorium is electrolyzed through a thorium halide bath and plated onto a metal cathode. The cathode metal and the thorium form a low-melting alloy which drips from the cathode into a collecting weir.

A. De BOER IODIDE STUDIES

1. <u>Tracer</u> (T. A. Milne) - Previous reports contained data on a series of four de Boer iodide runs made at varying disk temperatures but with all other

conditions held constant. Analysis are now available for three of these runs and the results are presented in Table I. This table shows the fission product activities, per gram of Th, in the various phases. The five phases considered in each case are:

a. "Original Metal" — material (metal) prior to reaction with iodine.

b. "Disk to Exit Wash" — a water wash of all material which traveled past the thorium disk and condensed.

c. "Entrance to Disk Wash" — a water wash of the unreacted material plus a wash of all material which condensed before reaching the thorium disk.

d. "Disk Deposit" — the thorium disk on which the metal iodides deposited (only the weight of the deposit is shown).

e. "Unreacted Metal" — metal which did not react with the iodine during the run.

Because there was no measurable weight gain of the disk in run ThI-E, the total counts per minute of fission products are shown for this phase.

From Table I it is clear that the de Boer process effectively removes Cs, Sr, Ce, and the rare earths and Ru, confirming previously-reported results.[1] The elements Zr and Pa transfer as well or better than thorium. The uranium does not appear to transfer as well as thorium.

Other features of these results will not be discussed until the data on the run of highest disk temperature (1450 C) are available.

2. Spent Fuel (J. Chilton) - The apparatus for the continuation of the de Boer iodide method of processing thorium fuels, shown in Fig. 1, has been completed and has tested satisfactorily. This project has been halted until work on some of the other projects is completed. At such time, the results will be evaluated and the more satisfactory processes will be selected for further work. As a result, the apparatus has been secured so that it will be available for future work on this or other processes.

B. THE VOLATILIZATION OF URANIUM AND FISSION PRODUCTS FROM MOLTEN AND SOLID THORIUM — URANIUM ALLOY

1. Introduction - The vacuum distillation of metal mixtures has been suggested as a method of processing spent reactor fuels. The large differences in

TABLE I

DISTRIBUTION OF THORIUM, URANIUM, AND FISSION PRODUCTS IN THREE DE BOER IODIDE EXPERIMENTS

Run	Phase	Thorium (gms)	Uranium Activity (%)	Relative Concentration in cpm/gm of Th for Each Phase						
				Fission Products						
				Cs	Sr	Ce	Y+R.E.**	Ru	Zr	Pa
ThI-C	Original metal	0.80	2.9	1.6	2.8	38.	2.0	1.9	2.5	44.
	Disk to exit wash	1.64	0.69	2.7	0.10	1.7	0.45	*	0.044	0.79
	Entrance to disk wash	0.122	53.	7.4	56.	590.	34.	3.0	39.	340.
	Disk deposit (@1300 C)	0.64	1.0	*	0.047	0.063	0.036	*	1.9	67.
	Unreacted metal	0.70	2.8	1.7	3.0	73.	4.3	1.7	2.9	39.
ThI-D	Original metal	0.92	3.1	1.7	4.6	30.	1.9	1.5	3.4	9.9
	Disk to exit wash	1.87	0.89	1.3	0.043	0.27	0.18	0.032	0.080	0.30
	Entrance to disk wash	0.160	35.	6.3	57.	350.	18.	27.	41.	109.
	Disk deposit (@1150 C)	0.11	2.5	*	0.82	0.9	*	0.32	4.6	35.
	Unreacted metal	0.68	3.1	1.9	4.5	26.	1.8	1.8	3.4	10.
ThI-E	Original metal	0.70	3.0	1.7	2.7	42.	3.1	1.1	2.4	17.
	Disk to exit wash	1.81	0.37	1.7	0.0077	0.66	0.33	*	0.17	3.3
	Entrance to disk wash	0.176	26.0	4.5	32.	180.	31.	1.2	14.	80.
	Disk deposit (@1000 C)	0.00	16.4†	*	*	0.017††	0.08††	*	1. ††	11. ††
	Unreacted metal	6.56	3.0	1.7	2.9	37.	3.4	1.2	1.3	19.

*Quantity insufficient for radiochemical detection.

†Quantity in mg in lieu of per cent because there was no measurable weight gain of the disk.

**Yttrium (major portion) plus rare earths other than Cerium.

††Cpm/gm x 10^{-4}

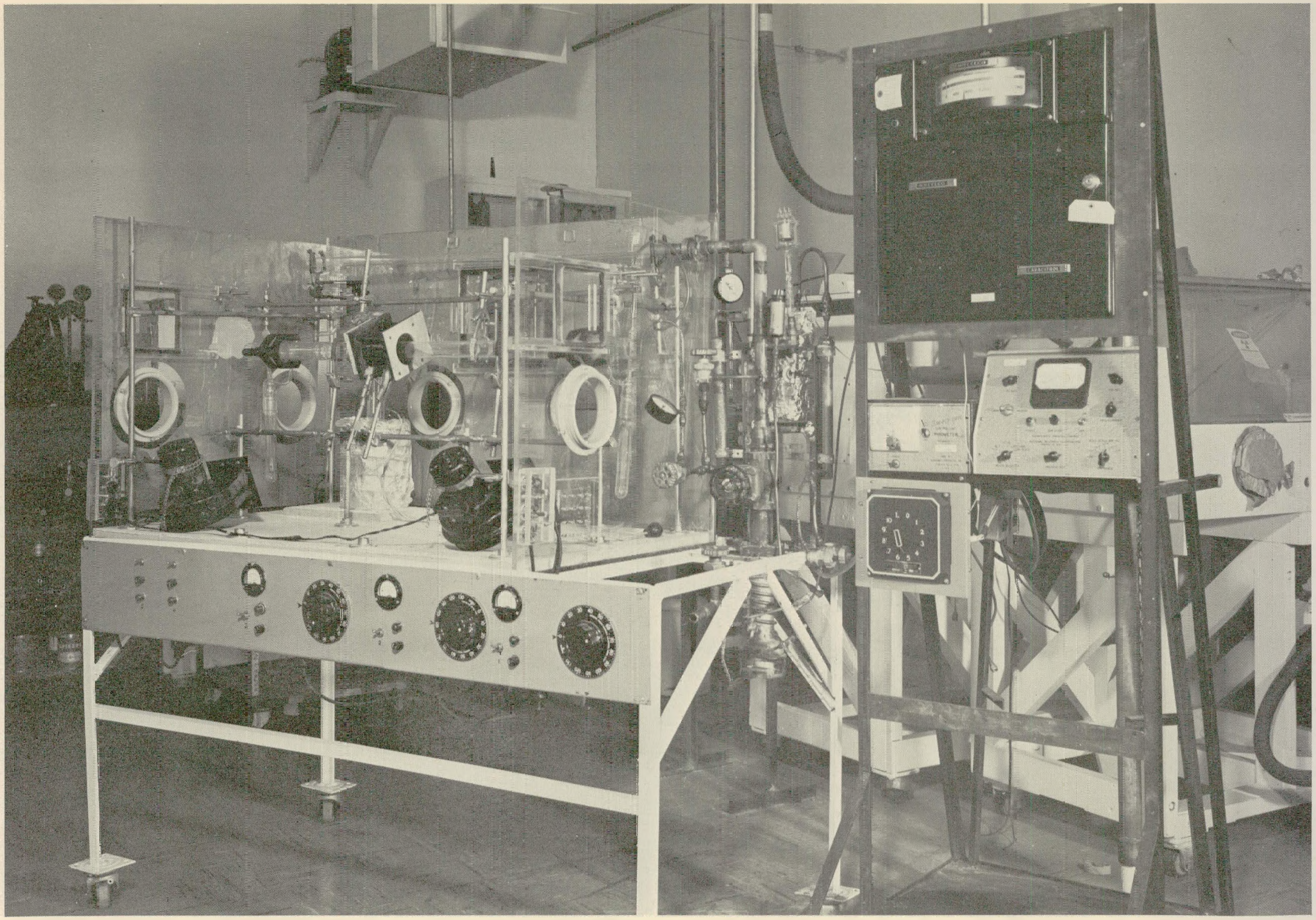

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Fig. 1. De Boer Apparatus

volatilities of metals Th and the fission product and the fact that the fuel may remain in the metallic state throughout the processing make such an approach attractive.

The theoretical rate of volatilization of Pu from U has been computed by Rosser[2] and experiments on irradiated uranium fuel have been carried out by Cubicciotti.[3] The results of the Pu volatilization experiments agree reasonable well with calculations based on the applicability of Raoult's law. It is indicated, therefore, that application of this process to liquid metal solutions may be feasible for large-scale Pu separation. A general treatment of the principles of vacuum distillation of metal mixtures has been given by J. E. Vivian.[4]

The vacuum distillation of metal constituents from thorium metal fuels appears promising since the vapor pressure of Th is lower than the vapor pressure of uranium. Thus higher temperatures could be employed to remove the volatile fission products such as Ce, rare earths, Sr, and Cs. The separation of U from Th, however, would be expected to be less efficient than the separation of Pu from U. Available vapor pressure data indicate that whereas the ratio

$$\frac{(P_o)_{Pu}\ (@\,1900\ K)}{(P_o)_U\ (@\,1900\ K)} = 500, \text{ the ratio } \frac{(P_o)_U\ (@\,2250\ K)}{(P_o)_{Th}\ (@\,2250\ K)} = 20$$

Table II presents the vapor pressure of substances of interest in the present study.

TABLE II

MELTING POINTS AND TEMPERATURES OF Th, Pa, U, AND FISSION PRODUCT ELEMENTS AT VARIOUS PARTIAL PRESSURES

	Temperature, °K				
Element	Melting Point	10^{-6} atm	10^{-5} atm	10^{-4} atm	Reference
I_2	386	241	260	282	11
Cs	302	383	425	476	11
Te_2	726	655	700	758	11
Sr	1044	740	810	900	11

TABLE II (Continued)

Element	Temperature, °K				Reference
	Melting Point	10^{-6} atm	10^{-5} atm	10^{-4} atm	
Ce	-	1690	1860	2070	9
Y	-	1530	1680	1870	9
U	1409	1990	2180	2400	8
Zr	2400	2070	2250	2450	11
Th	1978	2250	2450	2700	11
Pa	-	2250	2450	2700	11
Ru	2700	2480	2670	2900	11
Mo	2870	2530	2740	3000	11
Nd	2770	2820	3050	3340	11

In this investigation an attempt was made to determine the extent of volatilization of uranium and fission products from molten and solid irradiated Th-(3 w/o)U alloy. The experimental results are compared with theoretical calculations based on Raoult's law.

2. Equipment and Procedure - Samples of neutron-irradiated (nvt = 10^{17}) Th-(3 w/o)U alloy were melted in a well-shielded tantalum crucible contained, under vacuum, in a Vycor tube. The vacuum system was placed in a glove box to prevent scattering of contamination should the Vycor tube break during the heating cycle. Figure 2 is a photograph of the equipment and Fig. 3 is a schematic diagram of the essential parts.

The platform on which the crucible rested, and the shields covering the crucible, were made from five-mil tantalum sheet. The crucible was also shielded by wrapping with two-mil tantalum foil. These shields (Fig. 4), which were slotted to minimize inductive heating losses, protected the Vycor tube from heat radiating from the crucible, thus permitting the attainment of high crucible temperatures with only forced-air cooling of the Vycor tube.

A six-kilowatt Ajax-Northrup high-frequency converter was used to furnish power for heating the sample. An optical pyrometer was used to measure the temperature of the molten metal by sighting through a prism, a sight window, and a sight hole in the shielding. Corrections were added to the optical pyrometer readings to correct for absorption by the optical sight system and for the emissivity of the metal surface.

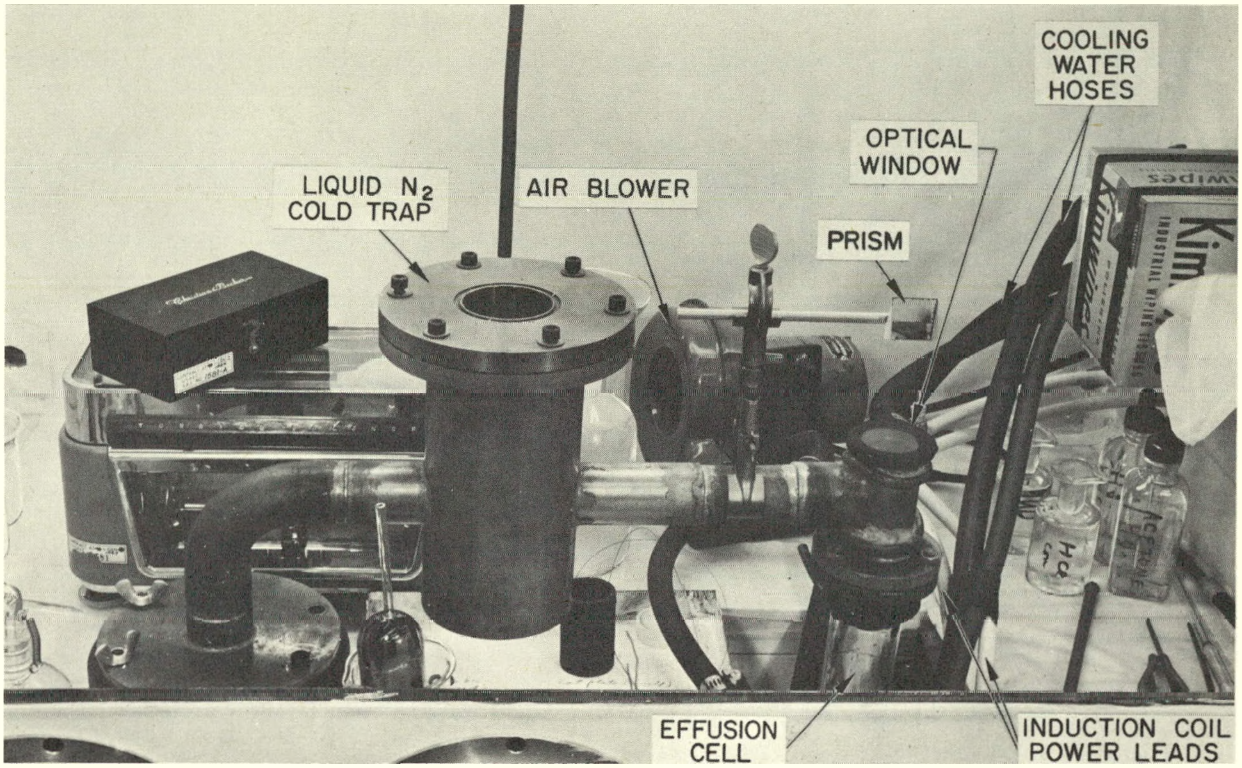

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Fig. 2. Volatilization Equipment

Tantalum was chosen as the crucible material for this volatilization study because it could withstand the high temperatures necessary to melt the alloy and because it would minimize scavenging of fission products. However, tantalum is known to be slightly soluble in thorium metal. A metallurgical examination of thorium metal melted in a tantalum crucible at approximately 1800 C for 10 minutes shows a dendritic phase in the cooled thorium metal. Figure 5, in the bright field, shows particles of tantalum evolving from the surface of the tantalum crucible as well as a dendritic pattern. Figure 6, polarized light, confirms the fact that the white particles in Fig. 5 are tantalum. An X-ray diffraction analysis of these particles indicate that they are tantalum metal plus a trace of TaC. When thorium metal, or Th-U alloy which had been melted in Ta, was dissolved, a black insoluble residue remained. This was determined by X-ray diffraction and fluorescence to be Ta plus some TaC; thorium was not detected.

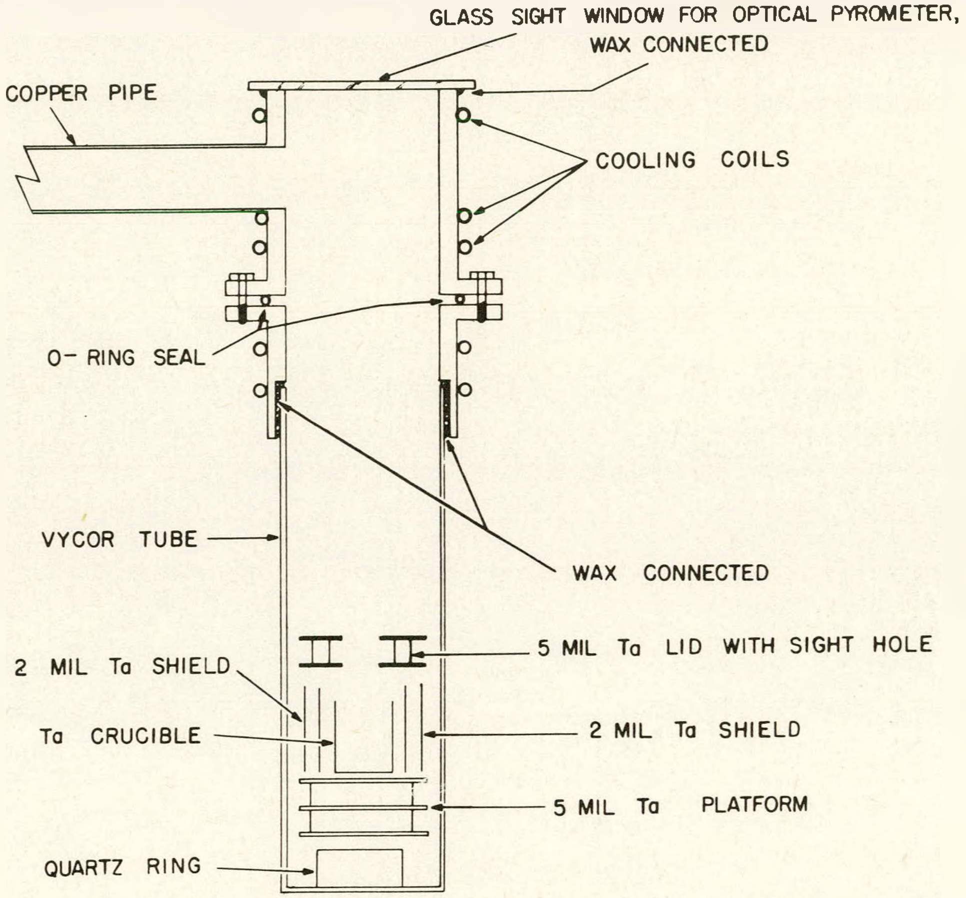

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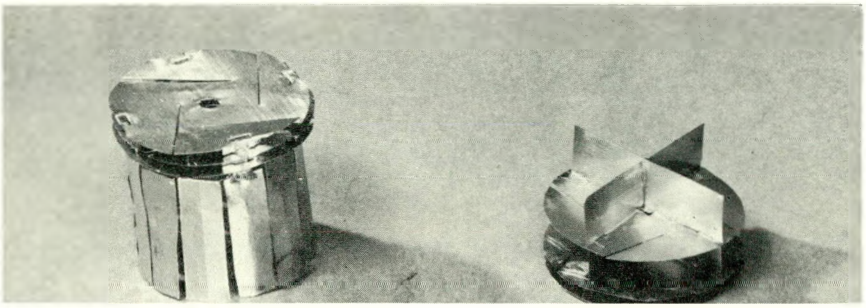
Fig. 3. Volatilization Chamber

The treated metal was dissolved for analysis in concentrated HNO_3, made 0.02 M in F^- ions. The Vycor tube and tantalum shielding were thoroughly washed with acids to recover as much of the volatilized fission products as possible. The solutions of products from each phase were analyzed and compared with that from a control phase of metal irradiated at the same time but untreated except for chemical dissolution. No analysis for U in the volatile phase was made.



TOP SHIELDS &
SIGHT HOLES

STAND & COVER
SHIELDS

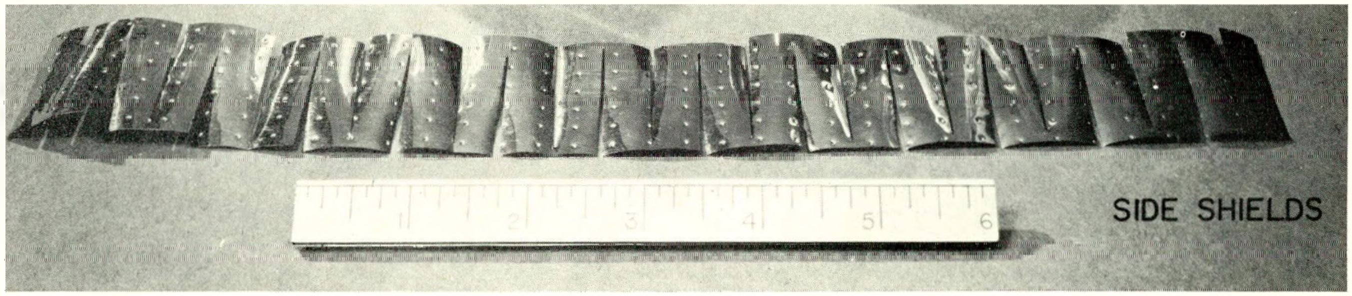


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Fig. 4. Radiation Shields

Three of the factors studied which affect volatilization rates were temperature, time of heating, and surface area-to-weight ratio of sample. The experimental program for liquid thorium is outlined in Table III.

In addition to these runs employing the Th-U in the molten state, two runs were made using solid Th-U alloy. It is not unreasonable to suppose that near the melting point, the diffusion of fission products through the solid might be sufficiently rapid to effect a separation by volatilization. The chief advantage of such a method would lie in the elimination of the container corrosion problem. An increased surface-to-mass ratio of the Th-U might be attained by hydriding and dehydriding the alloy prior to the volatilization. Both runs were of two hours duration and the temperature was maintained from 50 to 100 C below the melting point of the alloy. In one of the runs a solid cube of irradiated alloy having an area-to-weight ratio of 0.8, was placed in a Ta crucible. In the other run, the Th-U was hydrided and dehydrided, producing a sort of gravel which was stable

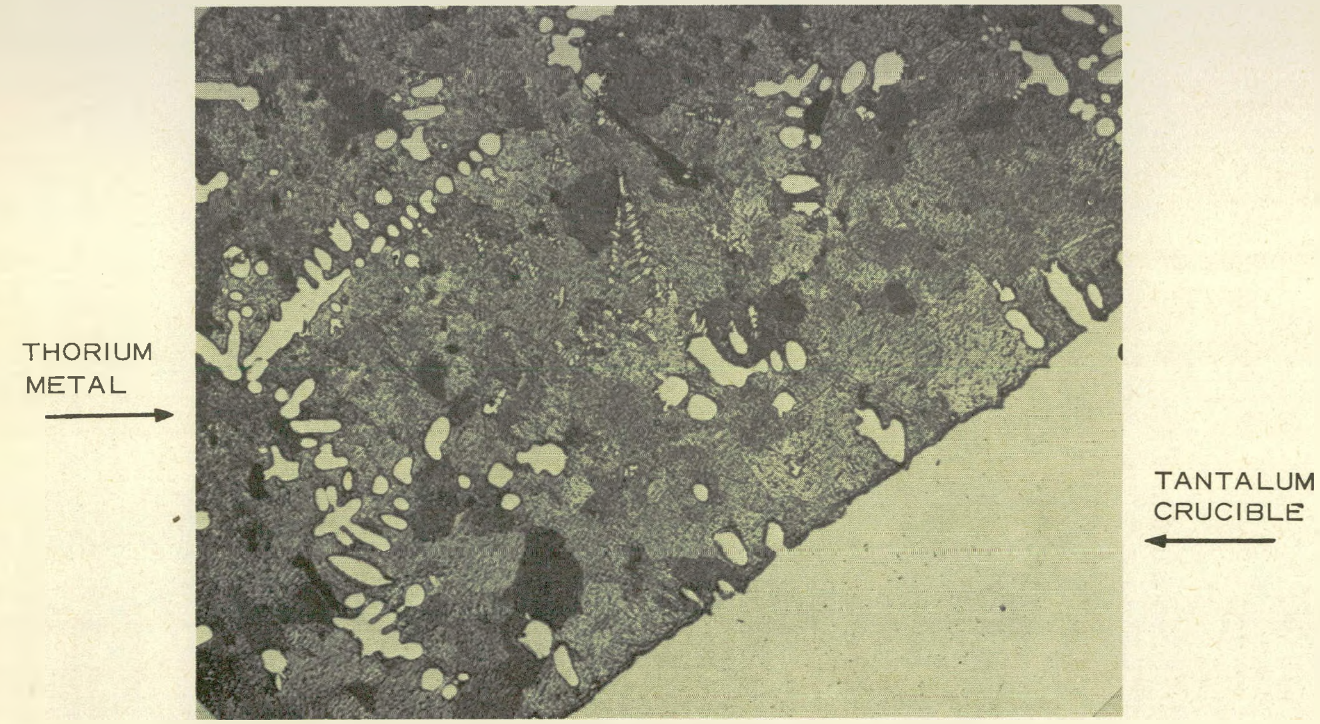

Fig. 5. Contact Area Molten Th Contained in Ta (Bright Field)

Fig. 6. Contact Area Molten Th Contained in Ta (Dark Field)

in air at room temperature. It was estimated that the area-to-weight ratio of the metal was approximately 10, although no surface area measurements were made.

TABLE III

PROGRAM OF VOLATILIZATION STUDIES FROM LIQUID THORIUM

Program	Variables		
	$\frac{\text{Area (cm}^2\text{)}}{\text{Wt (gms)}}$	Temperature, °C	Time (min)
Series I	0.4	1700	30
	-	1910	-
	-	2070	-
Series II	0.2	1910	30
	0.4	-	-
	0.7	-	-
Series III	0.4	1910	10
	-	-	30
	-	-	120

Figure 7 shows the fraction of U volatilized <u>vs</u> that expected from calculations (similar to those of Rosser[2]) based on Raoult's law.

<u>3. Results and Discussion</u> - In applying Rosser's equations to the present experiments, the following consideration was added. The rate of volatilization of a substance from a crucible with a lid containing a very small, infinitely-thin-edged orifice (ideal Knudsen cell) is simply related to the vapor pressure of the substance. However, as the orifice area becomes an appreciable fraction of the molten metal surface area, the reflection coefficient, α, affects the rate of effusion of material through the orifice. Likewise, as the thickness of the orifice increases, the fraction of the vapor which enters the orifice but is reflected back to the crucible interior increases.

In the present experiments an open crucible was used in which the molten Th-U covered the entire bottom surface. This experimental arrangement is essentially equivalent to a Knudsen cell in which the orifice has the same diameter as the crucible and a thickness equal to the length of the crucible.

Clausing,[5] Whitman,[6] Motzfeld,[7] and Thorn[8] have treated theoretically the rate of vaporization from a nonideal Knudsen cell. Their results indicate that, for the above experimental system, the equilibrium vapor pressure P_{eq} is related to the measured vapor pressure P_m by a relation which reduces to

$$P_m \frac{(1 + \alpha)}{(\alpha)} = P_{eq}$$

for the case of a crucible having a diameter equal to its length. Assuming that α is 1, which is probably true for most metals, $P_{eq} = 2\,P_m$. Thus, in our experiments the rate of escape of materials from the crucible is only about one-half the rate of vaporization from the metal surface. This correction was incorporated in Fig. 7 by using an effective evaporating area of just one-half the actual area of the melt. The results obtained for the volatilization of fission products and uranium from molten Th-U are presented in Tables IV, V and VI.

Of the various fission products for which analysis could be made, it would be expected that virtually all of the Cs, Sr and Te would volatilize under present conditions; the data in Table VI show that this was indeed true for Cs and Sr. As in other experiments, the behavior of Te is anomalous. The reported vapor pressures of Ru and Nb are so low that one would expect no significant removal. The vapor pressure of Pa is estimated to be the same as for Th so that no separation would be predicted. The vapor pressure of Zr is only slightly lower than the reported value for Th.

Figure 7 shows the fraction of uranium removed from the Th-U melt as a function of (A/W) t, the area-to-weight ratio times the time. The data show a considerable scatter but indicate that, at the lowest temperature, considerably more U volatilizes than expected while, at the highest temperature studied, somewhat less than the theoretical amount of U volatilized. At the intermediate temperatures, where most of the runs were made, the results are about what would be predicted from the reported vapor pressure of U.

TABLE IV

FISSION PRODUCT VOLATILIZATION FROM MOLTEN THORIUM-URANIUM SERIES I: VARIABLE, TEMPERATURE

Experimental Conditions			Fission Product or Element	Per Cent Activity of Phases Recovered		
Temp °C	$\frac{A}{W}$	Time (min)		Metal After Volatilization	Volatilized Material	Total*
1700	0.4	30	Ce	56	25	81
			Y+R.E.†	46	37	83
			Sr	0	93	93
			Pa	78	0	78
			Cs	6	86	92
			Te	49	48	97
			Ru	98	0	98
			Zr	86	0	86
			U	91	-	-
1910	0.4	30	Ce	30	29	59
			Y+R.E.†	16	47	63
			Sr	0	66	66
			Pa	81	0	81
			Cs	0	85	85
			Te	14	73	87
			Ru	78	0	78
			Zr	90	0	90
			U	89	-	-
2070	0.4	30	Ce	19	78	97
			Y+R.E.†	9	87	96
			Sr	0	80	80
			Pa	72	0	72
			Cs	0	90	90
			Te	0	76	76
			Ru	73	0	73
			Zr	80	0	80
			U	82	-	-

*Variations from 100% represents analytical inaccuracies.

†Y+R.E. = rare earths other than Ce (major portion = Y).

TABLE V

FISSION PRODUCT VOLATILIZATION FROM MOLTEN THORIUM-URANIUM

SERIES II: VARIABLE, AREA/WEIGHT

Experimental Conditions			Fission Product or Element	Per Cent Activity of Phases Recovered		
Temp °C	$\frac{A}{W}$	Time (min)		Metal After Volatilization	Volatilized Material	Total*
1910	0.2	30	Ce	75	27	102
			Y+R.E.†	36	52	88
			Sr	6	65	71
			Pa	84	0	84
			Cs	0	91	91
			Te	39	34	73
			Ru	91	0	91
			Zr	66	0	66
			U	99	-	-
1910	0.4	30	Ce	30	29	59
			Y+R.E.†	16	47	63
			Sr	0	66	66
			Pa	81	0	81
			Cs	0	85	85
			Te	14	73	87
			Ru	78	0	78
			Zr	90	0	90
			U	89	-	-
1910	0.7	30	Ce	15	84	99
			Y+R.E.†	17	72	89
			Sr	0	99	99
			Pa	82	0	82
			Cs	0	86	86
			Te	0	100	100
			Ru	67	0	67
			Zr	89	0	89
			U	99	-	-

*Variations from 100% represents analytical inaccuracies.

†Y+R.E. = rare earths other than Ce (major portion = Y).

TABLE VI

FISSION PRODUCT VOLATILIZATION FROM MOLTEN THORIUM-URANIUM

SERIES III: VARIABLE, TIME OF HEATING

Experimental Conditions			Fission Product or Element	Per Cent Activity of Phases Recovered		
Temp °C	$\frac{A}{W}$	Time (min)		Metal After Volatilization	Volatilized Material	Total*
1910	0.4	10	Ce	33	54	88
			Y+R.E.†	15	42	67
			Sr	0	93	93
			Pa	81	0	81
			Cs	0	95	95
			Te	8	45	53
			Ru	93	0	93
			Zr	99	0	99
			U	94	-	-
1910	0.4	30	Ce	30	29	59
			Y+R.E.†	16	47	63
			Sr	0	66	66
			Pa	81	0	81
			Cs	0	85	85
			Te	14	73	87
			Ru	78	0	78
			Zr	90	0	90
			U	89	-	-
1910	0.4	120	Ce	5	85	90
			Y+R.E.†	trace	101	101
			Sr	0	93	93
			Pa	76	0	76
			Cs	0	93	93
			Te	0	97	97
			Ru	91	0	91
			Zr	79	0	79
			U	78	-	-

*Variations from 100% represents analytical inaccuracies.

†Y+R.E. = rare earths other than Ce (major portion = Y).

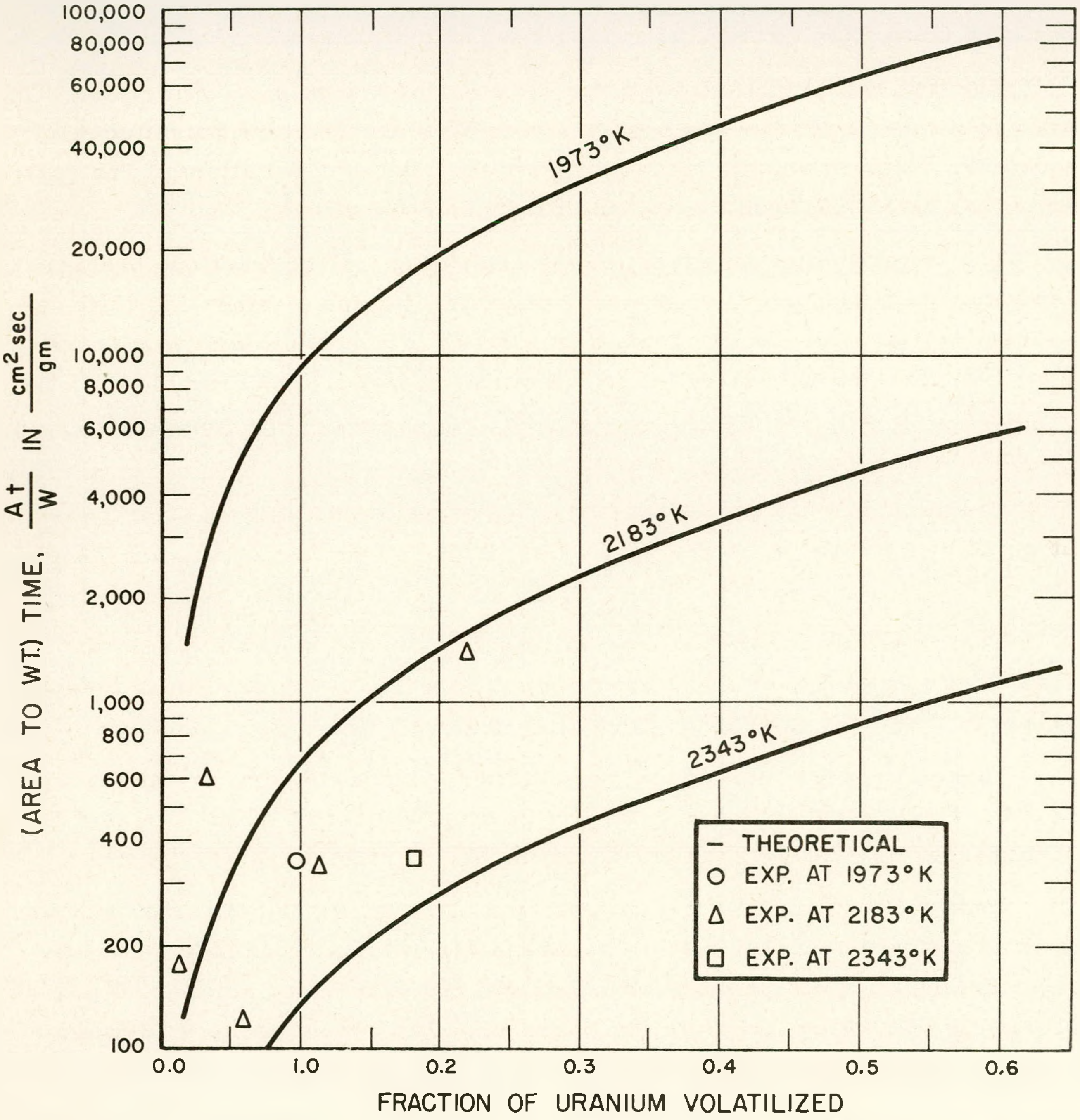

Fig. 7. Fraction of Uranium Volatilized vs That Expected From Calculations Based on Raoult's Law

The vapor pressure of Ce has recently been shown[9] to be intermediate between that of Pr and La, lying approximately two-thirds of the way toward La.[10] Using this estimate, the amount of Ce volatilizing is calculated to be about that predicted from Raoult's law.

The fission products listed under rare earths are primarily yttrium. The vapor pressure of yttrium has been shown to be about the same magnitude[9] as that for Pr,[10] therefore the values for Pr were used in calculations. The volatilization was much less than the 95 per cent or more predicted.

The factors which may tend to give low values for the fractions of these elements volatilized are: the presence of a film of oxide or other impurity on the metal surface, deviations from Raoult's law, and reflection of some of the volatile fission products from the shield sitting just above the crucible back into the melt. The latter effect would be expected to be more pronounced for a volatile element such as Ce or yttrium than for U.

The amount of Th lost by volatilization during these runs was not determined but would be expected to be negligible from Brewer's estimated vapor pressure data.

The results of the two solid volatilization runs are shown in Table VII. In each case three phases are distinguished: (1) the volatile phase, (2) the outer surface of the solid, and (3) the inner bulk of the solid.

These data seem to indicate that increasing the surface-to-weight ratio of the solid Th-U markedly increases the rate of volatilization of Cs, Sr, and Te but increases only slightly the volatilization of Ce or the other rare earths.

Some sintering of the Th-U gravel took place during the two-hour run so that it is not known to what extent Ce and the rare earths could be removed by longer heatings. These results with hydrided and dehydrided solid Th-U are sufficiently promising, however, to warrant further consideration of decontamination schemes involving solid Th.

4. Conclusions - These experiments have indicated that Cs, Sr, Te and an appreciable fraction of the Ce and other rare earths can be volatilized from molten Th contained in a Ta crucible. In this method however, the resultant Th will be contaminated with a definite but undetermined amount of Ta due to crucible attack. The use of a crucible more resistant to attack by molten thorium,

such as ThS, might allow essentially complete removal of Sr, Cs, Te, Ce and the rare earths without danger of crucible contamination. The elements Cs, Sr and Te can be removed from solid Th fuel provided that a large surface area-to-weight ratio is presented by a hydriding and dehydriding treatment. Cerium and the rare earths can be partially removed by such a process. Little or no crucible attack is anticipated by solid thorium.

The removal of U from Th by volatilization appears impractical due to the extremely high temperatures or long times of heating required.

TABLE VII

FISSION PRODUCT VOLATILIZATION FROM SOLID THORIUM URANIUM ALLOY

Test Conditions			Fission Product or Element	Per Cent Activity of Solid Th-(3 w/o)U After Volatilization	
Temp °C	$\frac{A}{W}$	Time (min)		Original Metal Not Hydrided (Single Cube)	Hydrided and Dehydrided (gravel)
1650	0.8	120	Cs	62	-
			Sr	58	-
			Te	100	-
			Y+R.E.*	60	-
			Ce	82	-
			U	-	-
1650	>10.	120	Cs	-	5
			Sr	-	1
			Te	-	1
			Y+R.E.*	-	48
			Ce	-	73
			U	-	98

*Y+R.E. = rare earths other than Ce (major portion = Y).

C. VOLATILIZATION OF FISSION PRODUCTS FROM ARC-MELTED Th-U ALLOY (R. A. Barney, W. Murbach)

Application of arc melting of irradiated Th-U alloy as an evaporation fission product decontamination procedure has continued. The arc-melting furnace has been described in previous reports of this series. Briefly, the furnace consisted of a water-cooled, movable, tungsten-tipped, molybdenum electrode and a water-cooled copper hearth. The whole system was enclosed within a glass cylinder, rubber-gasketed to steel, and connected to a vacuum system.

Power was supplied by a P&H dc arc-welding machine with a maximum output of 300 amperes.

Small samples of irradiated Th-(3 w/o)U alloy were arc melted under the condition summarized in Table VIII. Time intervals listed were exposure periods for one side of the metal button. Temperatures were measured with an optical pyrometer and are not corrected for absorption or emissivity. They are accurate to ± 150 C. Distribution data are also summarized in this table. These data demonstrate 66 to 94 per cent removal of cerium and rare earths, 80 to 90 per cent removal of cesium and strontium, 45 to 96 per cent decontamination of tellurium, and negligible evaporation of zirconium, ruthenium, and protactinium.

TABLE VIII

FISSION PRODUCT DECONTAMINATION - ARC-MELTING Th-(3 w/o)U ALLOY

Run	Time (min)	Temp. °C	Weight gms	Current Amps	Per Cent Activity of Fission Products							
					Ce	Re	Cs	Sr	Te	Zr	Pa	Ru
2	16	1650	2.85	19	25	52	99	100	20	0	*	1
4	21	1800	4.10	82	35	65	-	-	73	0	*	1
5	12	1900	2.51	60	85	78	95	99	89	0	31	*
6	10	1850	2.61	85	*	*	99	99	96	0	25	*
8†	8	1860	2.32	90	66	89	80	92	55	0	*	0
9†	8	1800	2.43	90	74	87	88	93	52	0	*	0
10†	8	1850	2.68	120	80	94	82	94	45	12	*	0

*Analysis at these points is being rechecked.
†20 milligrams of CaF_2.

D. SOLID AND LIQUID OXIDE SLAGGING OF Th-U ALLOY (N. D. Potter)

Evaluation of previous experiments concerning solid and liquid slagging of irradiated Th-U alloy is reported. Solid scavenging had been accomplished using ZrO_2 and ZrN crucibles at 1100 C to contain molten Th-U-Mn (88 - 3 - 9 per cent, respectively). Liquid slagging consisted of contacting, at 1700 C, an equimolar mixture of CaF_2-CaO with molten Th-(3 w/o)U alloy contained in a ThO_2 crucible. The data are presented in Table IX. The solid scavenging data disclose reasonably effective removal (32 to 69 per cent) of Ce, rare earths, Cs, and Sr, and poor decontamination (18 to 35 per cent) for Te, Ru and Zr. It was thought feasible that zirconium exchange played a role in the zirconium removal found in solid slagging. Liquid oxide - fluoride slagging data revealed 74 to 100 per cent removal of rare earths, Te and Sr as well as 56 per cent Zr and a small fraction of ruthenium.

TABLE IX

FISSION PRODUCT DECONTAMINATION OF IRRADIATED Th(3 w/o)U ALLOYS BY OXIDE SLAGGING

Weight of Th-(3 w/o)U (gms)	Temp. °C	Time (min)	Salts	Per Cent of Fission Product Activity Removed								
				Ce	Y+R.E.*	Cs	Sr	Te	Zr	Pa	Ru	U
28	1100	45	ZrO_2	32	57	28	69	18	35	6	21	29
28	1100	45	ZrN	36	39	56	61	32	-	40	40	44
3	1700	45	CaO_2-CaF_2	-	76	-	99	74	56	16	23	20

*Y+R.E. = rare earths other than Ce (major portion = Y).

E. FUSED SALT - MOLTEN Th-U ALLOY EQUILIBRATION (W. McKee and A. G. Buyers)

Experiments involving nonirradiated thorium-uranium alloy have been carried out using a frozen salt bed procedure for contacting melt components. Briefly, this method consisted of inductively melting the alloy which is supported by a bed of unmelted salt briquettes. The molten metal melts its salt environment as, under gravity, it proceeds downward through the frozen bed. After melting its way through the entire bed of frozen salt, the molten alloy drops from the induction field, and from the last salt briquette, into an alumina crucible and freezes immediately.

The salt bed for the first experiment was composed of analytical reagent-grade calcium fluoride. After preheating at 800 C for one-half hour, the salt was compressed under 8 to 10 thousand psi pressure into briquettes, 1.25 inches in diameter and above 0.75-inch thick. The briquettes were heated at 800 C for one-half hour and stored in a dessicator until needed.

The briquettes were stacked in a pile about six inches high and inserted into a Vycor tube which was open at both ends. Indenting the tube from the outside provided a stop which held the column about two inches from the bottom of the tube. A piece of the desired metal was laid on top of the bed. The assembly (Fig. 8) was then placed in a slightly-larger Vycor tube, closed at one end, which could be attached in a vertical position to a vacuum apparatus. The system was evacuated to 5 to 10 microns and then filled with argon which was purified by passing over uranium turnings at 600 C. After re-evacuation, the system was filled again with purified argon to a pressure of about 0.7 atmosphere.

The induction coil used to melt the metal was mounted on a support with a variable speed of vertical travel. The reaction tube extended downward through the center of the coil. The rate of rise or descent of the coil was directly controllable from 1/4 to 5 inches per minute; simple gear changes allowed other rates. The purpose of the movable support was to facilitate following the molten metal as it drops through the bed. Heating could be continued until the metal dropped out of the bottom of the bed, or terminated while the metal was still in the salt.

In one experiment, 17.574 gms of nonirradiated, 90 per cent Th - 10 per cent U alloy was heated by an Ajax converter operating at approximately 6 kw. The metal slug melted and moved slowly down through the salt bed leaving on the surface of the top briquette a black, glassy skull of approximately the same shape as the original metal. The course of the metal could be followed by watching the red flow through the sides of the salt bed. It was found that a quarter-inch rate of descent was too fast, but the coil was maintained in the proper position by occasionally stopping its downward movement. Heating was discontinued after

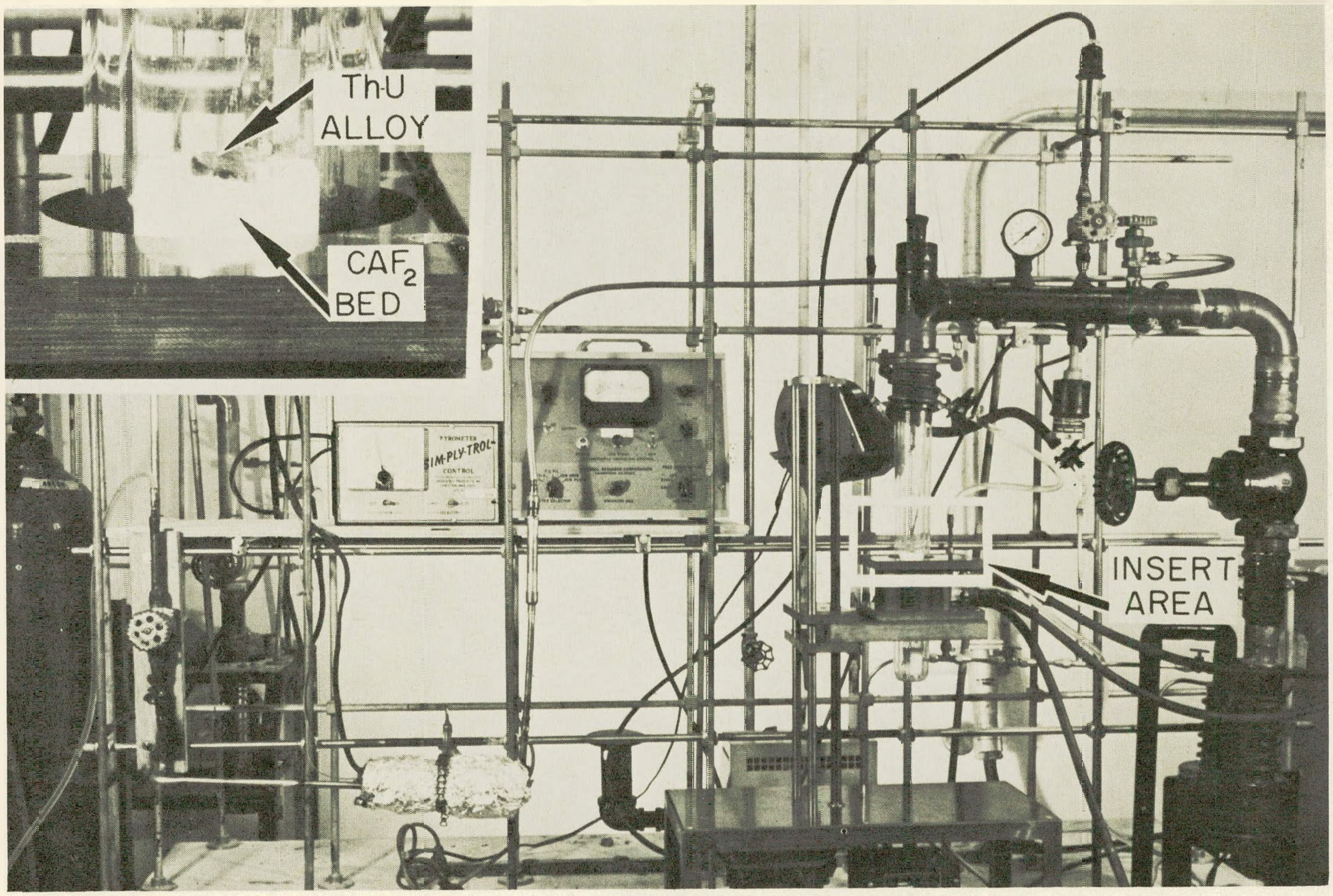

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Fig. 8. Salt Bed Assembly

approximately thirty minutes. The metal had moved downward about four inches and was still contained in the bed. When cool, the bed was removed and broken apart. It was found that the metal had formed into an approximate tear-drop shape, and had melted almost straight down through the salt leaving an open chimney of about one-quarter inch in diameter. The chimney was surrounded with a glassy, black, fused area about 1/16 to 3/16-inch thick. The metal broke away from its matrix very easily, leaving a bright metal surface. (The processed ingot and the processing frozen salt bed are shown in Fig. 9.) The weight loss of the treated alloy was 13.8 per cent.

In order to evaluate and understand the weight loss, a series of cold runs were made. It was found that loss of uranium to the salt bed was negligible, but 5 to 10 per cent of the thorium was removed. X-ray diffraction studies showed that the thorium was present in the salt bed as thorium fluoride.

A preliminary "hot" run has been made to study the removal of fission products from irradiated thorium-uranium alloys. A sample of Th-(10 w/o)U alloy irradiated nvt = 10^{17} was melted through a four inch bed of compacted CaF_2. Induction heating of the metal was at approximately 1700 C; the time of passage was 20 minutes. The results of the decontamination are shown in Table X.

TABLE X

FISSION PRODUCT DECONTAMINATION DATA - SALT BED PROCESS

Fission Product	Per Cent Removed From Processed Alloy
Ce	92
Y+R.E.*	90
Te	98
Sr	86
Cs	83
Pa	0
Zr	0
Ru	0

*Y+R.E. = rare earths other than Ce (major portion = Y).

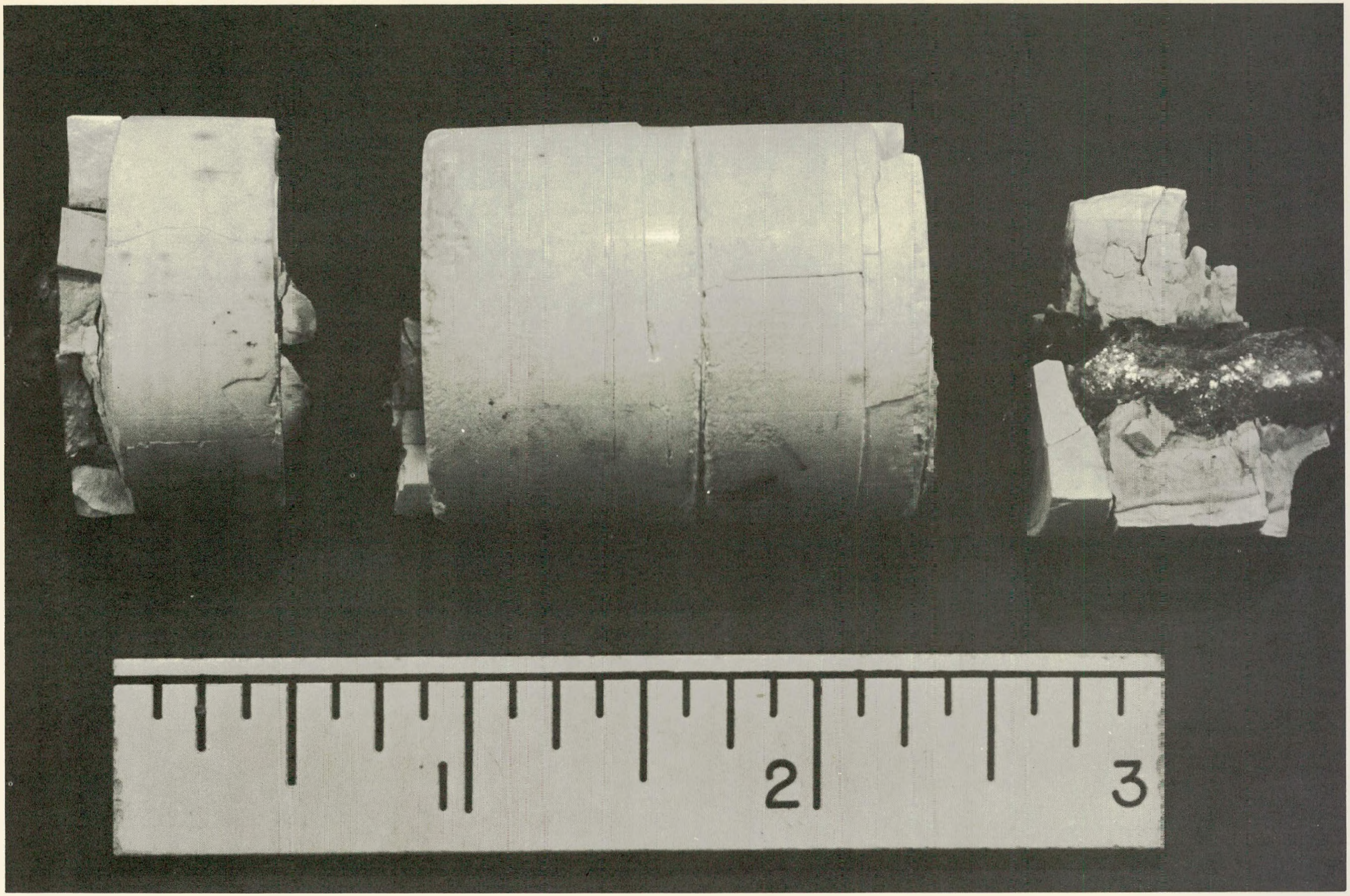

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Fig. 9. Salt Bed Processing

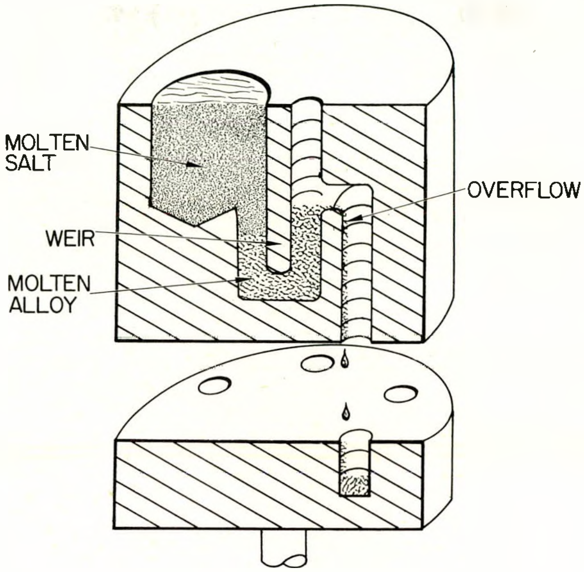

Fig. 10. Electrorefining Weir and Mold Assembly

F. ELECTROREFINING OF THORIUM FROM MOLTEN HALIDE BATHS
(R. A. Barney)

Electrorefining experience at KAPL has demonstrated excellent decontamination of irradiated uranium, particularly the more noble fission products such as ruthenium which is not normally removed in other pyrochemical processes.[12,13] In brief, this method consists of plating uranium from a fused salt bath onto a cathode, which at the temperature of the bath forms a eutectic with the uranium. The eutectic melts and drips off the cathode to overflow from a weir into molds below. (See Fig. 10.) If a manganese or nickel cathode is used, it is possible to volatilize the alloyed metal by arc melting, leaving relatively pure thorium.

The electrorefining method has these advantages: thorium may be used in any shape, limited only by the size of the anode basket; excellent decontamination is possible for all fission products; and container problems are considerably reduced since the thorium need not be melted.

The graphite cell was degassed in a vacuum at 1180 C and reheated to 1080 C in a helium atmosphere. The apparatus appears to function properly. Anhydrous salt mixtures, NaCℓ-ThCℓ$_4$ (60-40 w/o), for use as cell electrolyte have been prepared in the apparatus of Fig. 11.

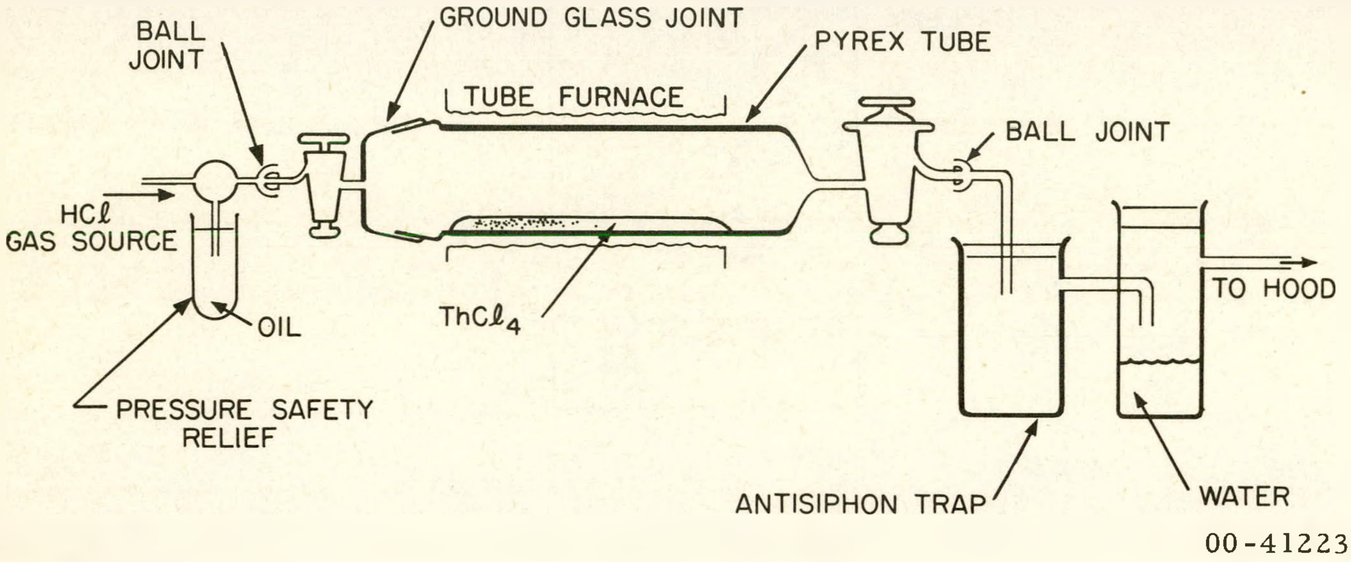

Fig. 11. Salt Drying Apparatus

A eutectic composed of Thorium and Manganese (12-1/2 per cent Manganese) was made. This eutectic, with a melting point of 980 C, seems to be satisfactory for filling the weir of the electrorefining crucible.

III. SUMMARY

Application of the de Boer iodide refining process to irradiated Th-(3 w/o)U alloy (nvt = 10^{17}) has been completed. The most recent data have demonstrated that this process will remove more than 90 per cent Cs, Sr, Ce, rare earths, and Ru, thus confirming previous results. Zirconium and Pa were transferred with thorium.

Apparatus has been constructed to be used with spent thorium fuel fragments; however, this effort has been tabled temporarily.

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