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LOW DECONTAMINATION REPROCESSING OF THORIUM-URANIUM ALLOYS BY INDUCTION DRIP MELTING

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ABSTRACT

The feasibility of low decontamination of thorium-uranium alloys by drip melting under vacuum in a high frequency induction field was investigated experimentally. A substantial portion of the rare earths as well as the more volatile fission products were removed and no detectable vaporization of thorium or uranium was found. Fission product removal was improved by extending the heating period, that is, by decreasing the drip rate. A satisfactory, completely remote handling system for in-cave experiments with irradiated fuel was developed.

The process shows promise for reprocessing of thorium-uranium fuels if 100 % decontamination is not required. The method's simplicity makes it readily adaptable to remote handling techniques, and power requirements are not excessive.

I. INTRODUCTION

The interest in thorium and thorium-uranium alloys as nuclear power reactor fuels, both as core material and in breeder blankets, is increasing rapidly. Reprocessing of these fuels will be required, and present concepts indicate that a high degree of decontamination may not be necessary. Low decontamination methods appear practical for thorium fuels, as the activity associated with thorium from which all fission products are removed is of sufficient level to require remote refabrication.[1]

As has been previously suggested,[2] direct volatilization of contaminants is attractive because of the high melting points, 1600°C and above, of thorium and thorium rich alloys. A study of available vapor pressure data tabulated below indicates that it should be possible to remove a considerable fraction of the more volatile fission products at temperatures slightly above the melting point of the thorium alloys. At the same time, loss of thorium and uranium should be negligible.

TABLE I

VAPOR PRESSURE OF REPRESENTATIVE ELEMENTS AT 2000°K[3]

Element	Vapor Pressure (atmospheres)
Cs	>1
Te	>1
Sr	>1
Ce	4×10^{-2}
La	10^{-3}
U	10^{-6}
Zr	$<10^{-6}$
Th	$<10^{-6}$
Pa	$<10^{-6}$
Ru	$<10^{-6}$

In view of the severe containment problem in handling molten thorium especially for extended periods, methods avoiding this difficulty have been sought. Drip melting, successfully employed in purifying zirconium and other metals,[4, 5] appeared suitable. In this process, the metal under study is suspended in an inert atmosphere or under vacuum, and is heated in a high frequency induction field. By suitable adjustment of frequency, induction coil design and power, melting at or near the surface of the metal, can be achieved at a controlled rate. The molten metal drips into a container and cools rapidly below the melting point, minimizing reaction with the container. Preliminary investigation showed the method to be feasible, and this study was undertaken to determine the degree of decontamination obtainable. At the same time, engineering development of a completely remote operation, adaptable to pilot plant or semi-production scales for reprocessing of irradiated fuel by drip melting, was initiated.

II. EXPERIMENTAL METHOD

A. EQUIPMENT AND PROCEDURE

A description of the supporting facilities for the remote operations on the irradiated alloy has been detailed in a previous report[6]. All of the experiments on irradiated Th - 9w/o U alloy were performed in the modified hot cave facility. A part of the hot cave facility, such as the permanent upper box, portable lower box, fluid manifold, and the manipulators, may be seen in Figure 1.

The major vacuum furnace components are shown in Figure 1, and further details in Figure 2. All experiments were performed under vacuum ranging from 10^{-4} to 10^{-5} mm Hg. The vacuum system consists of a fore-pump, diffusion pump, cold trap, cesium trap, mold chamber, quartz tube assembly, and vacuum indicating gauges. The cesium trap, a dc electrostatic precipitator assembly, was not used, since it was not warranted by the activity level of the experimental samples.

High frequency power is brought in from the electronic generator by a coaxial cable, through flexible water-cooled leads to the induction heating coil. The coil is positioned at the fuel slug tip with the hydraulic piston at the right, as shown in Figure 2. To raise the quartz furnace tube, the piston is further extended above the positioning pin to engage and lift the tube at the top flange. The tube and coil are then rotated away together making the mold chamber accessible, while the vulnerable quartz tube is firmly supported at all times.

The fuel specimen, attached to a quarter-inch diameter cold thorium rod and cross bar, is brought in from the top by the manipulator. The vacuum flanges are all "O"-ring joints fitted without bolting, and are easily removed and replaced by the manipulators.

Temperature control has been visual, aided by power control data acquired on cold runs. Results for a given power setting and induction coil were found to be remarkably reproducible. In practice, it has been found best to bring the temperature up rapidly, until the tip begins to flow or elongate, then to reduce the power to the desired setting. The sample can be held just below the melting point or with the lower end in a plastic state for four to five hours without actually dripping.

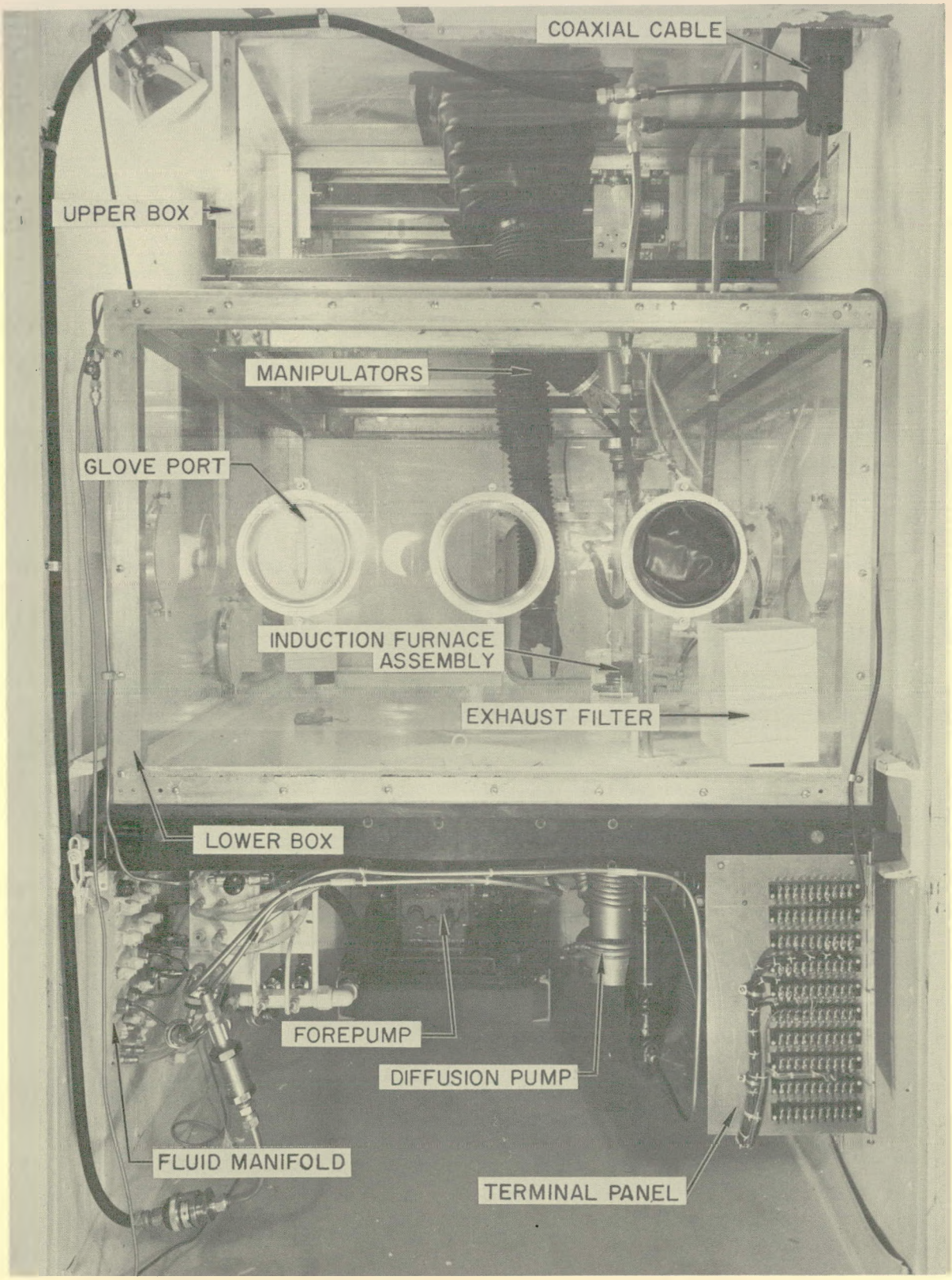

Figure 1. Vacuum Furnace Components in the Hot Cave

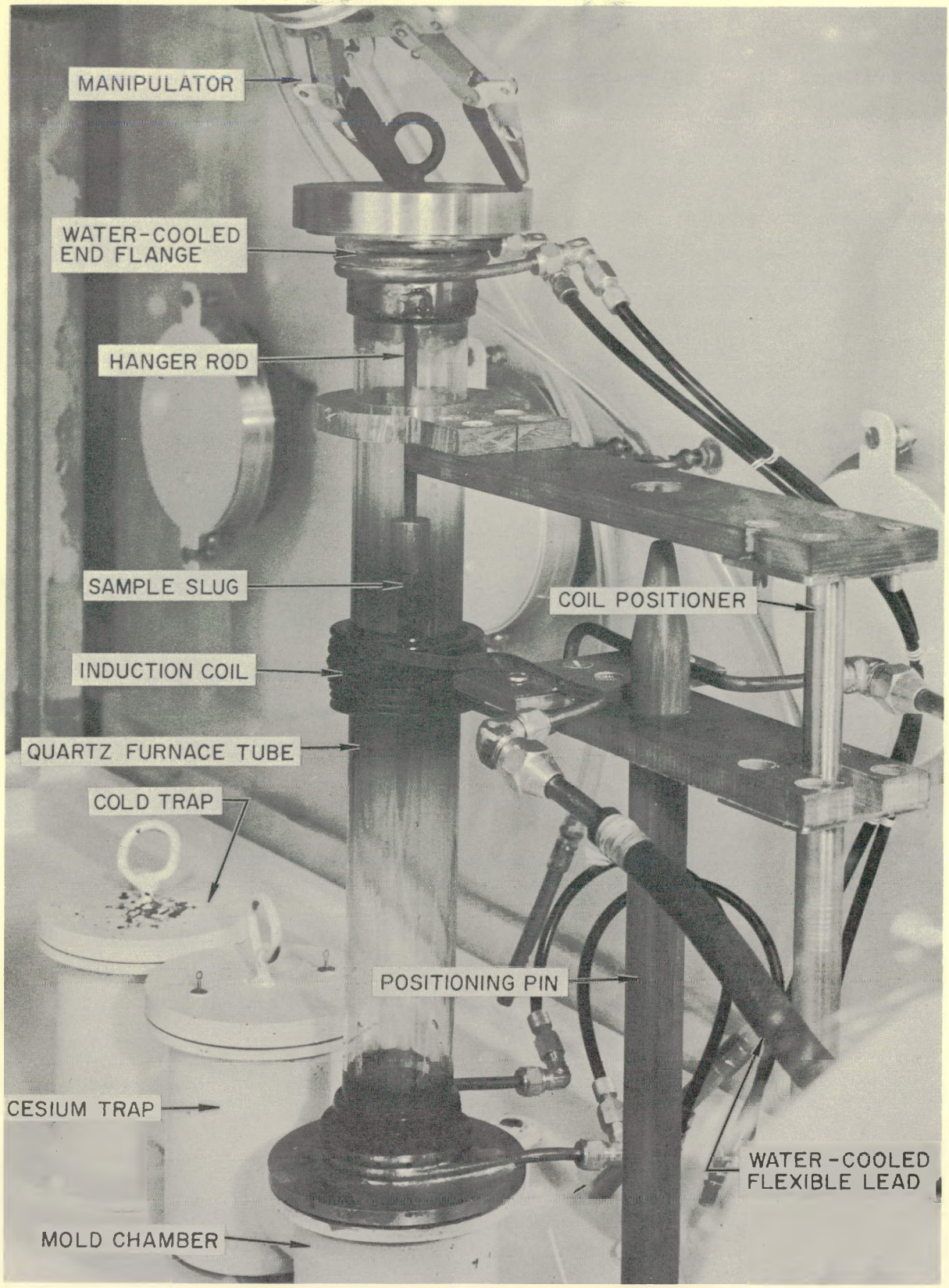

Figure 2. Closeup of Induction Furnace Assembly After Drip Melting

On experiments with radioactive samples, the remotely filled liquid nitrogen cold trap was used, and a vacuum of 2 to 5 x 10^{-5} mm Hg was consistently maintained.

The vacuum system, as well as the box atmosphere, were connected to the hot cave exhaust through filters. At the end of each experiment the furnace was allowed to cool for several hours under vacuum to minimize escape of particulate matter when the furnace was opened and samples and molds were removed. Graphite, copper and stainless steel molds were used with no particular advantage noted for any one of them.

B. WELDING OF THORIUM FUEL SLUGS BY INDUCTION HEATING

One of the anticipated problems in the drip melting experiment was the development of a satisfactory method for suspending the irradiated fuel in the vacuum furnace. For cold work this problem was solved by the simple technique of tapping the specimen and threading a tantalum hanger rod. Later, a thorium rod was used to avoid contamination by a foreign metal. Samples for irradiated fuel were tapped in this manner.

This makeshift method was not considered practicable for reactor fuels. Resistance welding such as flash or stud-welding seemed promising but required additional apparatus. It was therefore decided to try induction welding, using the drip melting apparatus and power supply. This method proved satisfactory. Two slugs are mounted vertically in the quartz furnace tube, one simply resting on the other; the system evacuated, and the joint heated to 1200-1400°C for about 10 minutes. No visible flow of metal occurs, but radiographs show complete fusion across the interface, and a tensile strength of 44,000 psi was found in the only specimen tested. This result is within 10% of the yield point of the parent metal. No special joint preparation is required, simply clean, squared surfaces. The cold slug is tapped for attachment of a 1/4-inch thorium hanger rod. The weld can be made with the same coil and 350 kc power supply used for drip melting, so that auxiliary equipment is not needed.

Figure 3 shows a typical welded joint after drip melting. Originally the two slugs were approximately the same length. When the power was turned off, no perceptible color gradient could be observed at the interface.

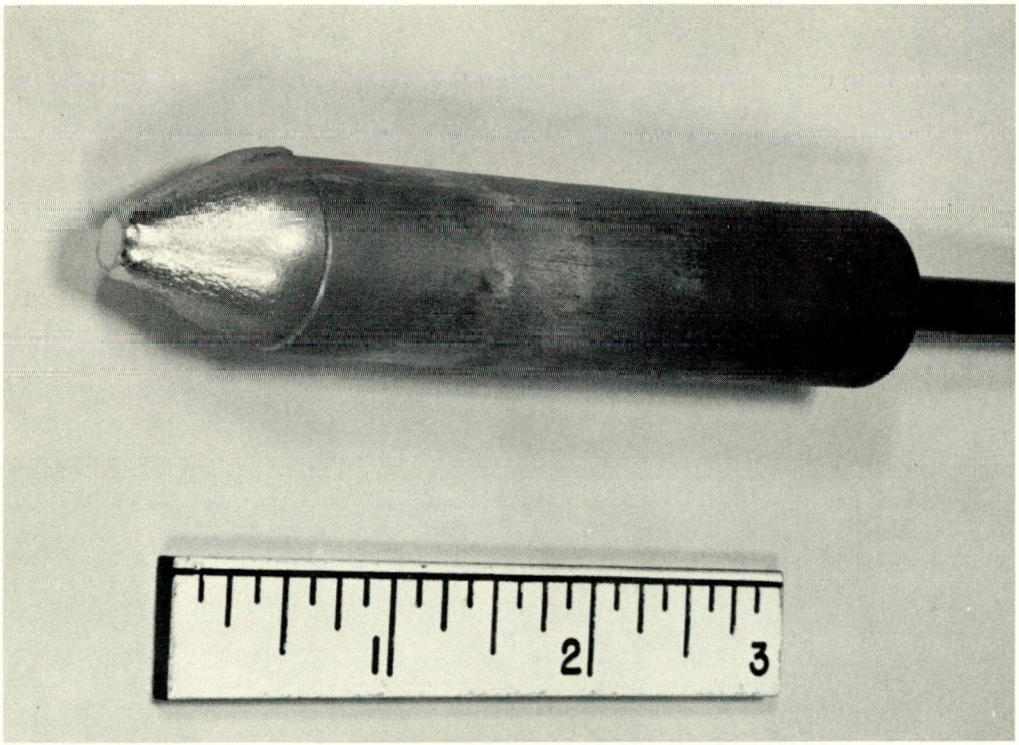

Figure 3. Welded and Drip Melted Thorium-Uranium Alloy Rod

C. INDUCTION HEATING SYSTEM

The first experiments in drip melting of thorium - uranium alloys were made with a 6 kw spark-gap converter at a frequency of about 36 kc. Two experiments were carried out, using this power supply and samples of irradiated Th - 3w/o U alloy (10^{17} nvt). While it was possible to melt the alloys with this power source, the frequency was not high enough for efficient drip melting.

The depth of penetration of the eddy currents causing the heating is inversely proportional to the square root of the frequency[7]. Due to radiation losses from the surface and conduction toward the center, the center tended to melt first. This resulted in the escape of an occasional droplet, which usually froze as an icicle on leaving the hottest zone.

A 20 kw electronic generator with a frequency range of 300-450 kc proved more suitable. Reducing effective current penetration by a theoretical factor of 3.0 to 3.5, approximately the square root of ten, apparently resulted in surface melting. With careful power control, a smooth flow of molten metal occurred.

A slowly elongating tip developed, which could be dripped or held in a plastic state as desired.

Coil design has not been found difficult. The practice has been to construct coils as needed, rather than to purchase them. Current concentrators were experimented with, and may be used to advantage if intense local heating is required. In general, it has been found desirable in experimental work to provide an ample power supply to take care of mismatches and loss of efficiency. Also radiation shields can be eliminated, thus simplifying design and improving visibility.

A coaxial cable was designed and fabricated to bring high frequency power from the electronic generator into the hot cave. The cable was run overhead from the generator through the roof of the cave, a total length of 28 feet, and was constructed of copper water tube and fittings using soldered joints throughout. The 2-inch outer tube is air cooled; the 1/2-inch inner tube, water cooled. This arrangement proved to be satisfactory without modification. Power losses at full power are about 1.0 kw and 0.2 kw in the inner and outer tubes respectively.

Power consumption is dependent chiefly on the length of the heating period. It was found that total power input in holding the lower end, about an inch in length, of a 3/4-inch diameter slug at the melting point was about 7.5 kw; and that an increase in power of 5% was sufficient to initiate dripping at a slow rate. On the basis of a 4-hour preheating period, and a drip rate of two grams per minute thereafter, a standard slug 6 inches long and of approximately 500 gms can be melted in about four hours more. This amounts to about 8 kw x 8 hrs/0.5 kg. = 128 kw hrs/kg. At ten mills per kw hr, the cost of power for decontamination by drip melting becomes about $1.25/kg. The cost of simply melting the alloys is much less. The power input was 11 kw at a rate of 30 grams per minute. With the same power cost of ten mills per kw hr., this amounts to $0.06/kg.

No attempt was made to minimize power losses in these experiments. On a production basis, with close attention to impedance matching, high frequency power transmission line losses and efficient radiation shielding, power requirements can be reduced at least 50% and probably more.

After satisfactory testing of the in-cave apparatus with unirradiated metal, a series of experiments was carries out using irradiated Th - 9w/o U alloy.

III. RESULTS AND DISCUSSION

A. PRELIMINARY DECONTAMINATION STUDIES

As previously mentioned, preliminary feasibility studies, made by using a 6 kw, 36 kc spark-gap converter, were not completely successful, due to the difficulties encountered in melting. Data obtained in two experiments are shown in Table II.

TABLE II

RESULTS OF PRELIMINARY STUDIES ON IRRADIATED Th - 3w/o U ALLOY

(Power source - 6 kw 36 kc spark-gap converter)

	% Decontamination							
Expt	Sr	Cs	Ce	R.E.	Zr	Pa	U	Th
1	72.5	30	4	11	0	2	0	0
2 *	57.0	61	8	11	–	–	–	–

*No. 2 slug held at approximately 1400°C for 3 hours, sample cut from rod.

The results are, in general, in accordance with predictions from vapor pressure data. The removals are quite low, indicating that the low power, low frequency converter is not satisfactory for drip melting.

B. IN-CAVE DECONTAMINATION STUDIES

A total of seven hot runs was made in the hot cave using the remote operation equipment and procedure developed for this work. All of these experiments were made at a frequency of 325 or 420 kc, using Th - 9w/o U 3/4-in diameter fuel slugs irradiated to an integrated flux of 8.7×10^{17} nvt, and cooled 60 to 80 days. Results are shown in Table III.

It will be noted that prolonged heating of the irradiated fuel greatly improved fission element removal. In addition to the time factor, diffusion was no doubt greatly improved by maintaining the elongated tip in a plastic state, and by presenting fresh metal at the surface continuously.

TABLE III

RESULTS ON IRRADIATED Th - 9w/o U ALLOY

(Power source - 20 kw 300-450 kc electronic generator)

Run No.	Heating Time (min)	Frequency (kc)	% Decontamination			
			Sr	Cs	RE	Ce
1	<1.0	325	60	56	9	0
2	1.0	325	59	50	17	3
3	1.5	325	45	31	11	3
4	240.0	325	96	88	64	27
5	300.0	325	92	88	55	25
6	1.5	420	42	14	20	17
7	7.0	420	45	79	33	3

The higher frequency employed in Runs No. 6 and 7 did not appear beneficial for this particular alloy.

Removal of over 50% of the rare earths on Runs No. 4 and 5, where prolonged heating was employed, is considered promising. The more volatile fission products such as strontium and cesium were also readily removed during the longer heating runs.

Zone diffusion of thorium and uranium in the alloy was observed from the irradiated thorium-uranium analyses, and has been checked using a normal thorium-uranium sample. Uranium diffuses into the hot zone during heating, and the concentration increases with the length of the heating period.

Ruthenium analyses of the drip melted samples indicate that on the two runs in which the slug was subjected to prolonged heating before melting, a considerable diffusion of ruthenium into the hot zone occurred. The ruthenium concentration in these drip melted samples increased by a factor of about four compared to the original slug and the short runs. See Table IV. Protactinium analyses showed a similar trend, but less pronounced.

The majority of the fission products volatized in the experiments collected on the inner surface of the quartz furnace tube in a thin dark-colored layer near the heating zone. Following the hot experiments, the film on the liquid nitrogen

cold trap was dissolved and checked for total activity. The film's activity was negligible compared to the total activity of the quartz tube, which indicates low contamination of the vacuum components.

TABLE IV

DIFFUSION BY INDUCTION HEATING OF RUTHENIUM AND PROTACTINIUM IN IRRADIATED THORIUM-URANIUM ALLOY

	Activity in counts/min/gm	
	Ru (x 10^6)	Pa (x 10^8)
Control	0.46	0.97
Run No. 1	0.60	0.96
Run No. 2	0.47	0.91
Run No. 4	2.20	1.10
Run No. 5	1.70	1.10

C. MISCELLANEOUS EXPERIMENTS WITH UNIRRADIATED ALLOYS

1. Pure Thorium

One experiment was carried out in which a 1-inch diameter unalloyed thorium fuel slug was melted. No change in power requirements was noted, but dripping characteristics were markedly different, apparently due to decreased surface tension. A thin film of metal melted rapidly, tended to run down the circumference of the slug, and dropped off immediately in very small droplets. Thus, fuel composition may have an important bearing on drip melting operations.

2. Thorium and Uranium Vaporization Study

Routine weight balances in the course of experiments indicated no loss of uranium or thorium during drip melting. To verify this, a careful check of weights and composition was made in connection with another experiment. About two inches of a 3/4-inch diameter thorium-uranium sample was melted at a rate of about 30 gm per minute, after prolonged heating close to the melting point. The overall weight balance of original weight versus melted plus unmelted alloy checked to 0.03% and thorium-uranium balances also checked within 0.1% indicating no apparent volatilization or pick-up of foreign material.

3. Casting and Remelting of Drip Melted Alloys

An obvious objective and advantage of the drip melting process lies in obtaining sound castings directly from drip melted metal. To date, only limited effort has been devoted to this problem, and no really satisfactory castings have been obtained.

Rapid induction remelting of imperfect castings or even of scrap in a non-suscepting container offers another approach. A number of zirconia, alumina and mullite right-cylinder crucibles was tested. Fairly good castings with slight surface contamination were obtained. Two such castings are shown in Figure 4. In each case the crucibles were filled with unirradiated Th - 9w/o U drip melted scrap and heated rapidly under vacuum to the melting point. The power was shut off just after the sample melted to prevent contamination of the sample by the crucible. A major difficulty encountered was the cracking of the crucibles under thermal shock. Slow preheating of the crucibles might overcome this problem.

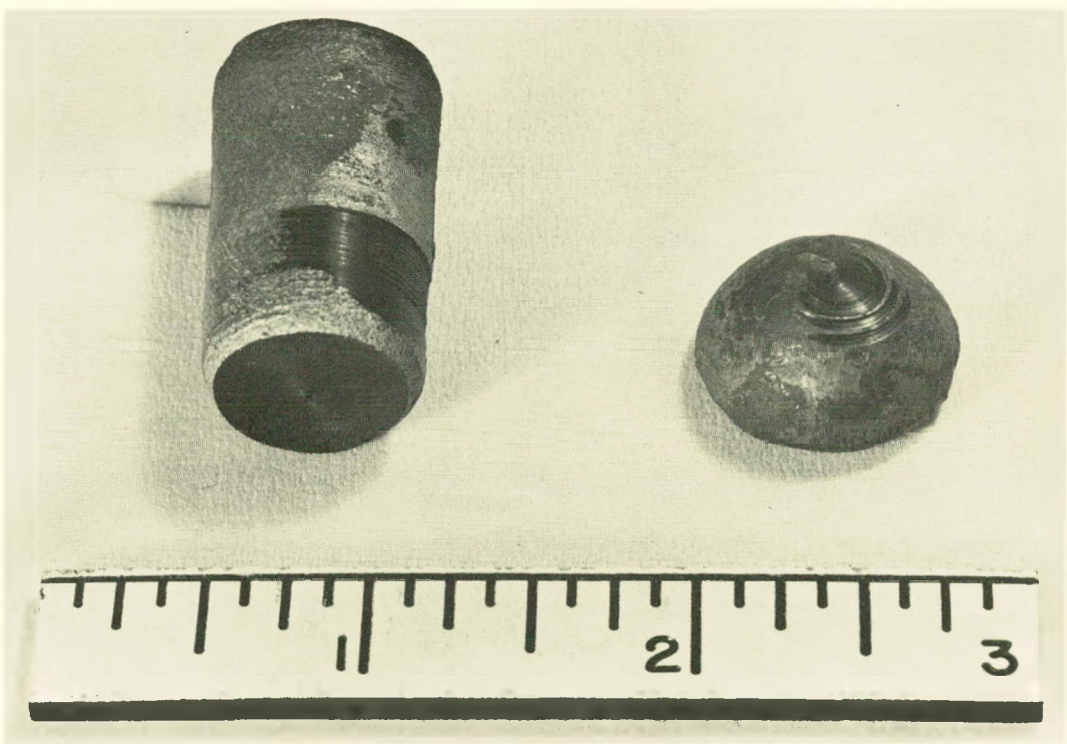

Figure 4. Thorium-Uranium Alloy Castings

IV. CONCLUSIONS

The feasibility of induction drip melting of irradiated thorium-uranium alloys by remote methods has been demonstrated. Fission element removal by volatilization has in general been in agreement with vapor pressure data. A substantial portion of the rare earths as well as the more volatile fission products can be removed by drip melting. The refractory metals are not removed. Loss of thorium and uranium is negligible.

The process appears promising from an engineering standpoint, as the operations are readily adaptable to remote handling. Power costs in melting the alloys are moderate.

This process would be applicable to a reactor such as a single region breeder, where it is not necessary to separate bred uranium from a thorium matrix.

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