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23 PAGES
METALLURGY AND CERAMICS

FISSION PRODUCT SEPARATION FROM THORIUM-URANIUM ALLOY BY ARC-ZONE MELTING

BY:
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TABLE OF CONTENTS

		Page No.
	Abstract	5
I.	Introduction	7
II.	Experimental	7
	A. Equipment	7
	B. Procedures	9
	C. Analyses	10
III.	Results	11
	A. Distribution of Fission Products	11
	B. Discussion	20
IV.	Conclusions	22
	References	23

LIST OF TABLES

I.	Summary of Conditions for Arc-Zone Melting of Irradiated Thorium-Uranium Alloy	10
II.	Ratio: Activities Observed After Melting/Activities Before Melting for Run I (Th-3w/oU at 2 inches/hour)	12
III.	Ratio: Activities Observed After Melting/Activities Before Melting for Run II (Th-3w/oU at 1/2 inch/hour)	12
IV.	Ratio: Activities Observed After Melting/Activities Before Melting for Run III (Th-16w/oU at 1/2 inch/hour)	13

LIST OF FIGURES

		Page No
1.	Arc-Zone Melting Machine	6
2.	Arc-Stabilizing Mechanism	8
3.	Movable Hearth	8
4.	Arc-Zone Melted Specimen	8
5.	Uranium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy	13
6.	Cerium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy	14
7.	Yttrium and Rare Earths Distribution in Zone Melted Irradiated Thorium-Uranium Alloy	15
8.	Tellurium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy	16
9.	Zirconium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy	17
10.	Protactinium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy	18
11.	Ruthenium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy	19
12.	Redistribution of Four Elements in Bar I	20
13.	Redistribution of Four Elements in Bar II	21
14.	Redistribution of Four Elements in Bar III	22

ABSTRACT

An experimental investigation was made to determine the feasibility of removing fission products from irradiated thorium-uranium alloys by using a zone-melting process. This process utilizes an electric arc to maintain the molten zone. Radiochemical analyses of the processed alloys indicated that uranium, tellurium, zirconium, and ruthenium were successfully moved in the direction of zone travel, and that some of the fission products were removed during processing by volatilization.

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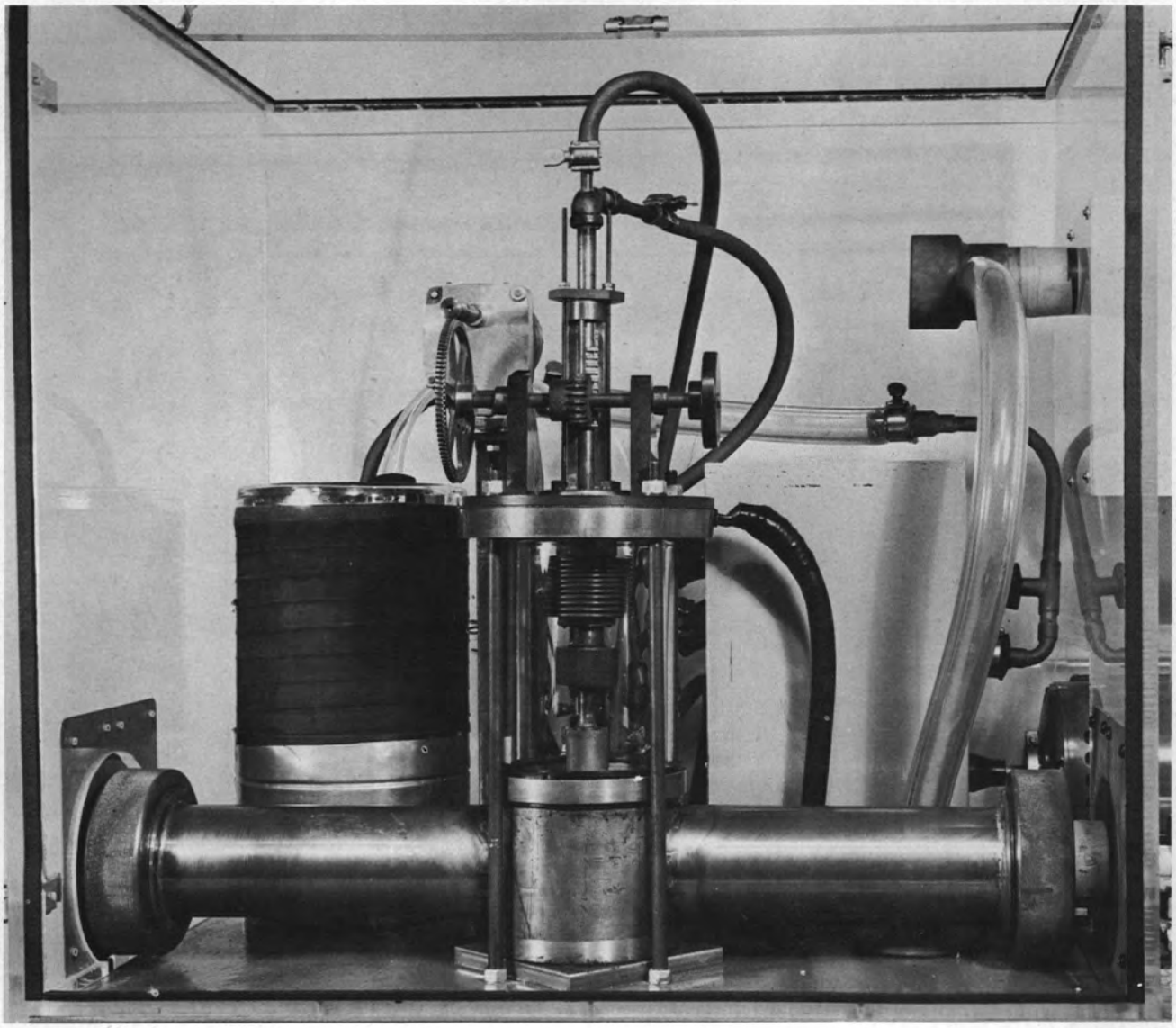

Fig. 1. Arc-Zone Melting Machine

I. INTRODUCTION

The work described indicates the effectiveness of a zone-melting process for fission product removal from solid Th-U reactor fuels. Zone melting of uranium has been investigated elsewhere.[1, 7, 8, 9, 10, 11, 12] Purification of material by zone melting has been reported on by W. G. Pfann and others.[1, 2] The zone melting consists of passing a source of heat along the length of a material specimen so that a molten region travels through the specimen in one direction. If there is a solubility difference between the liquid and solid state for a particular solute, the movement of the solid-liquid-solid interfaces may cause a redistribution of the solute due to diffusion and transport processes. Theoretical concepts can be found in metallurgy literature.[2, 3, 4, 5, 6] Successful purification has been achieved elsewhere in such materials as germanium, silicon, antimony, and tin.

II. EXPERIMENTAL

A. EQUIPMENT

The equipment and techniques used have been described previously.[13] The machine illustrated in Fig. 1 utilizes a dc arc to maintain the melted region, Fig. 2. In this respect the machine is novel compared to others which normally employ resistance or induction heating devices.

A metal bar rests on a water-cooled copper hearth, see Fig. 3, which passes under the arc at a predetermined rate. Contamination of the molten metal is minimized, since it is not necessary to use a crucible. The development of a contamination-free crucible, usually needed for processing of molten uranium and thorium, is a severe metallurgical problem which is avoided in this application. A surface barrier, analogous to that between oil and a drop of water in the oil, exists between the liquid metal and the cold hearth, isolating the molten region from the hearth. Continuity of the molten zone is maintained by surface tension and cohesive forces existing between it and the solidified pieces of metal on either side. A processed bar is shown in Fig. 4.

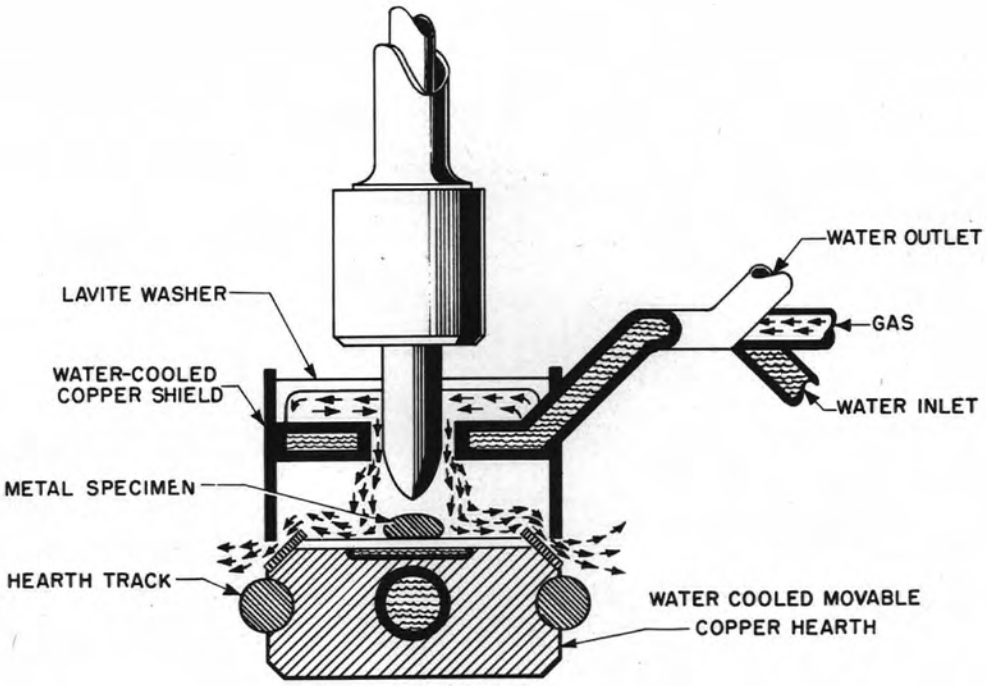

Fig. 2. Arc-Stabilizing Mechanism

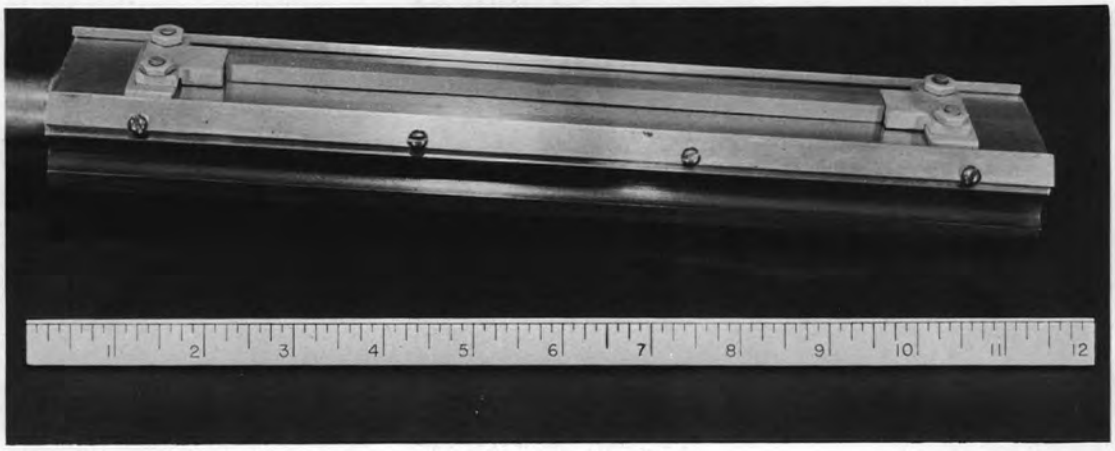

Fig. 3. Movable Hearth

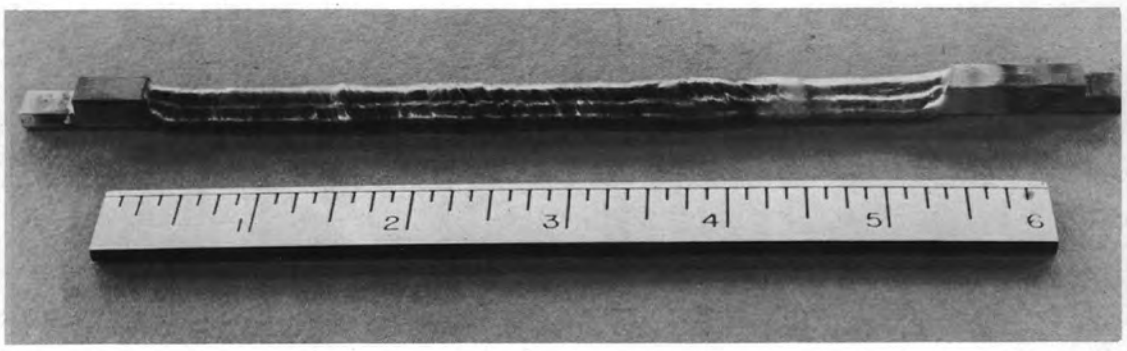

Fig. 4. Arc-Zone Melted Specimen

B. PROCEDURES

Irradiated pellets of thorium-uranium alloy were placed in a row on the water-cooled hearth, within the arc zone melting machine. Unirradiated end pieces made of normal thorium were prepared and placed at each end of the row of pellets. A modification to help stabilize the arc, consisting of a water-cooled gas supply ring, prohibited the direct observation of the molten metal. It was found necessary from experience to fuse the loosely placed pieces into one bar by making several rapid passes under the arc. When this was not done initially, discontinuities developed during a slow pass. This was probably caused by the combination of the geometry of pellets in a row, the resultant uneven conductive heat transfer rate, and the existent cohesive forces acting together to form a void between pellets. Zone passes were made immediately after the assembled pieces were fused into a bar. Contamination from an inert gas atmosphere was kept to a minimum by employing the same purified argon atmosphere for initial fusing as well as for the zone-melting process. The conditions under which each of the bars were processed are described in the following paragraphs and indicated in Table I.

1. Specimen Number One - Twenty 1/4-inch cubes of thorium containing three weight-per cent uranium, which had been irradiated with 10^{17} nvt, were passed under the arc at the rather rapid rate of 2 inches/hour. The arc current was not measured during processing of this bar. A molybdenum electrode which was used was not satisfactory because it showed signs of erosion. Near the middle of the bar an enlarged lump formed which may have interfered with fission-product transport through that region. The total bar length, including the end pieces, was 6-3/4 inches.

2. Specimen Number Two - Twenty-four 1/4-inch cubes of thorium containing three weight-per cent uranium, irradiated with 10^{17} nvt, were assembled and processed. Six "zone" passes were made at 1/2-inch/hour. The total length of the bar was 9-3/4 inches. A 5-inch "zone-processed" length was cut into 1/2-inch pieces for analysis. Two of the 1/2-inch pieces were split to separate the top from the bottom, thus permitting a determination of the fission-product distribution between top and bottom of the molten area. An ammeter was used during this run. Incomplete melting occurred during the first pass; therefore,

the current was increased for the remaining passes. A newly developed tungsten-tipped electrode[14] was used which proved to be satisfactory.

3. Specimen Number Three - A thorium bar alloyed with sixteen weight-per cent uranium was prepared at an earlier date by passing an assembly of uranium foils and a thorium bar rapidly under the arc. The bar was sectioned, capsuled, and irradiated with 10^{17} nvt. Then it was re-fused into a bar in the zone-melting machine and given six passes at 1/2 inch/hour. This bar was smaller in cross section than the previous bars; therefore, an estimate had to be made of the new arc current requirements. The initial current setting proved to be too high and the bar severed at a point 1-1/4 inches from one end. After readjustment of the current, the 4-1/2-inch section remaining was successfully zone-processed. Analyses were made of the 4-1/2-inch section after it had been cut into 1/2-inch pieces.

C. ANALYSES

Conditions under which the three runs were made are summarized in Table I. The surface of each bar was etched with acid before the bars were sectioned for analysis. The etching was done with concentrated HNO_3 made 0.02 molar in fluoride ions by addition of ammonium bifluoride. Analyses were made of the etch solution for fission-product content. In this way information was obtained as to the presence of fission products on or near the surface.

TABLE I

SUMMARY OF CONDITIONS FOR ARC-ZONE MELTING OF IRRADIATED THORIUM-URANIUM ALLOY

Test Conditions	Run Number 1	2	3
Alloy	Th-3 w/o U	Th-3 w/o U	Th-16 w/o U
Diam. of bar (in.)	1/4	1/4	1/8
Length of analyzed melted area (in.)	5-1/2	5	4-1/4
Hearth speed (in./hr)	2	1/2	1/2
No. of passes	5	6	6
Electrode material	Molybdenum	Tungsten tipped Molybdenum	Tungsten tipped Molybdenum
Arc current (amp)	Not measured	65 to 90	50

The 1/2-inch pieces of the zone-processed bars, were also dissolved in concentrated HNO_3 made 0.02 molar in fluoride ions, and were analyzed for fission-product content. Radiochemical procedures were used for fission product separations, and in most cases, followed those of Coryell and Sugarman,[15] with revisions to yield final precipitates which were free of contamination by protactinium and thorium daughter products. Radioactive decay of the different elements was observed to verify the identity of the separated fission products.

In Runs II and III the copper hearth on which the specimen rested was swabbed to obtain a sample of material which had volatilized from the molten zone and condensed on the cold hearth. Full recovery of the material deposited on the furnace walls and parts was not attempted because of the complexity of parts. The electrodes also became radioactively contaminated but no attempt was made to analyze this activity.

III. RESULTS

A. DISTRIBUTION OF FISSION PRODUCTS

Fission-product contents and their distribution in each of the three processed bars are indicated in Tables II, III, and IV for the elements investigated. The following paragraphs contain a discussion of the redistribution of each element for the three runs. Graphs of the fission-product distribution for each element in the three respective runs are shown in Fig. 5-11. The concentrations, determined by analysis, are indicated as the ratio of the residual amount to the amount contained in an unprocessed control piece.

No preferential distribution of fission products was observed between the top and bottom pieces of Bar II.

1. Uranium (Fig. 5) - Uranium did not move at the rapid zone-rate of 2-inch/hour, but a noticeable redistribution did occur in each of the two bars run at 1/2-inch/hour. Based on considerations of the constitutional diagram of the Th-U system,[16] this increase of uranium concentration in the direction of zone movements is to be expected. According to this diagram, the region containing less than 20 per cent U has a liquidus with a negative slope, and if

TABLE II

RATIO: ACTIVITIES OBSERVED AFTER MELTING/ACTIVITIES BEFORE MELTING FOR RUN I

(Th-3w/oU at 2 inches/hour)

Increment Analyzed	Element								
	U	Cs	Sr	Ce	R.E.*	Te	Zr	Pa	Ru
0 to 1/2 in.	1.02	0.	0.	0.51	0.60	0.62	0.41	0.68	0.68
1/2 to 1 in.	1.01	0.	0.	0.67	0.74	0.50	0.50	0.87	0.91
1-1/2 to 2 in.	1.00	0.	0.	0.75	0.91	0.52	0.60	1.04	1.13
2-1/2 to 3 in.	1.00	0.	0.	0.78	0.80	0.57	0.58	1.02	1.42
3-1/2 to 4-1/4 in.	1.01	0.	0.	0.67	0.83	0.62	0.60	0.94	2.06
4-1/2 to 5 in.	0.37†	0.	0.	0.59	0.82	0.57	0.66	0.75	2.29
Surface etch	av of above	none	none	excess	excess	excess	av of above	less than av of above	less than av of above
Volatile phase**									

*Yttrium and rare earths.
†Approximately 1/3 of the melted area was Th-U Alloy. Approximately 2/3, from end pieces, was normal thorium.
**Not collected.

TABLE III

RATIO: ACTIVITIES OBSERVED AFTER MELTING/ACTIVITIES BEFORE MELTING FOR RUN II

(Th-3w/oU at 1/2 inch/hour)

Increment Analyzed	Element								
	U	Cs	Sr	Ce	R.E.*	Te	Zr	Pa	Ru
0 to 1/2 in.	0.74	0.	0.	0.67	0.51	0.32	0.91	0.73	0.05
1/2 to 1 in.	0.79	0.	0.	0.61	0.31	0.20	0.86	0.75	0.06
1-1/2 to 2 in.									
(Top Section)	0.89	0.	0.	0.59	0.34	0.24	1.28	0.51	0.24
(Bottom Section)	0.91	0.	0.	0.60	0.21	0.32	1.07	0.56	0.20
2-1/2 to 3 in.	0.94	0.	0.	0.50	0.22	0.77	1.19	0.53	0.39
3-1/2 to 4 in.									
(Top Section)	0.91	0.	0.	0.46	0.27	0.28	1.05	0.48	0.30
(Bottom Section)	0.70	0.	0.	0.42	0.23	0.35	1.24	0.60	0.26
4-1/2 to 5 in.	1.09	0.	0.	0.6	0.28	1.39	1.21	0.33	4.52
Surface etch	av of above	none	none	av of above	av of above	excess	av of above	excess	some
Volatile phase	none	excess	excess	av of above	excess	some	none	none	none

*Yttrium and rare earths.

TABLE IV

RATIO: ACTIVITIES OBSERVED AFTER MELTING/ACTIVITIES

BEFORE MELTING FOR RUN III

(Th-16w/oU at 1/2 inch/hour)

Increment Analyzed	Element								
	U	Cs	Sr	Ce	R.E.*	Te	Zr	Pa	Ru
0 to 1/2 in.	0.71	0.	0.	0.50	0.40	0.25	0.87	0.50	0.18
1 to 1-1/2 in.	0.86	0.	0.	0.66	0.51	0.42	0.97	0.61	0.28
2 to 2-1/2 in.	1.02	0.	0.	0.78	0.41	0.60	1.15	0.69	0.53
3 to 3-1/2 in.	1.17	0.	0.	0.82	0.46	0.86	1.14	0.88	1.36
3-1/2 to 4-1/4 in.	1.69	0.19	0.20	0.86	0.38	1.42	1.42	0.94	4.25
Surface etch	excess	trace	trace	av of above	av of above	av of above	av of above	av of above	excess
Volatile phase	none	excess	excess	av of above	av of above	none	none	none	none

*Yttrium and rare earths.

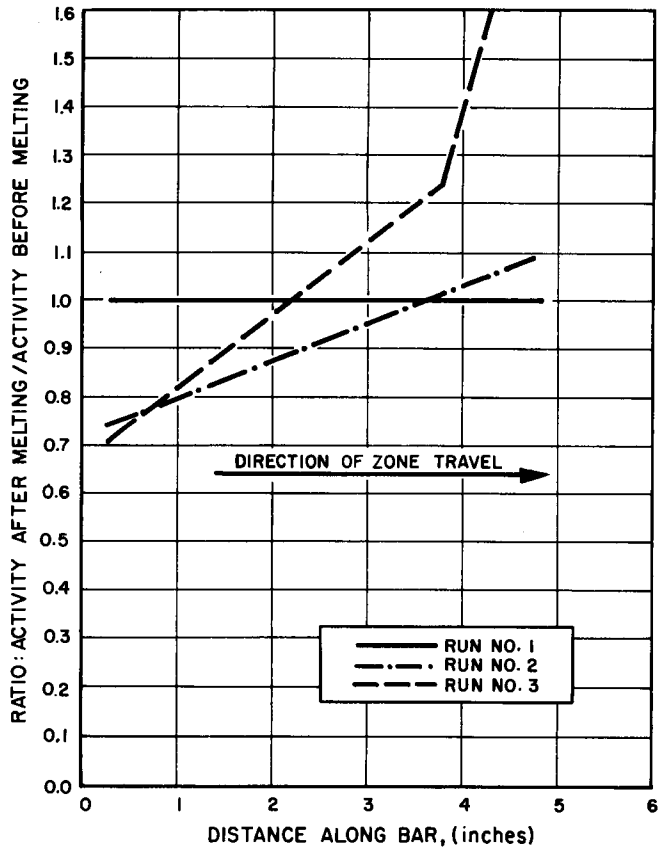

Fig. 5. Uranium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy

the solidus is assumed to have a negative slope, the zone processing should and did cause a transport of solute in the direction of zone travel.

2. Cesium and Strontium - These elements are omitted from graphic presentation because they volatilized completely. The data from the last 1/2-inch section of run III indicate one of two effects: 1) some migration of the elements, or 2) the arc-zone melt area was not carried to the same stopping place for the six passes, thus leaving part of the final area unmelted. This second explanation is the more logical because both cesium and strontium have been found to be completely volatilized at the temperatures required to melt thorium metal.[17]

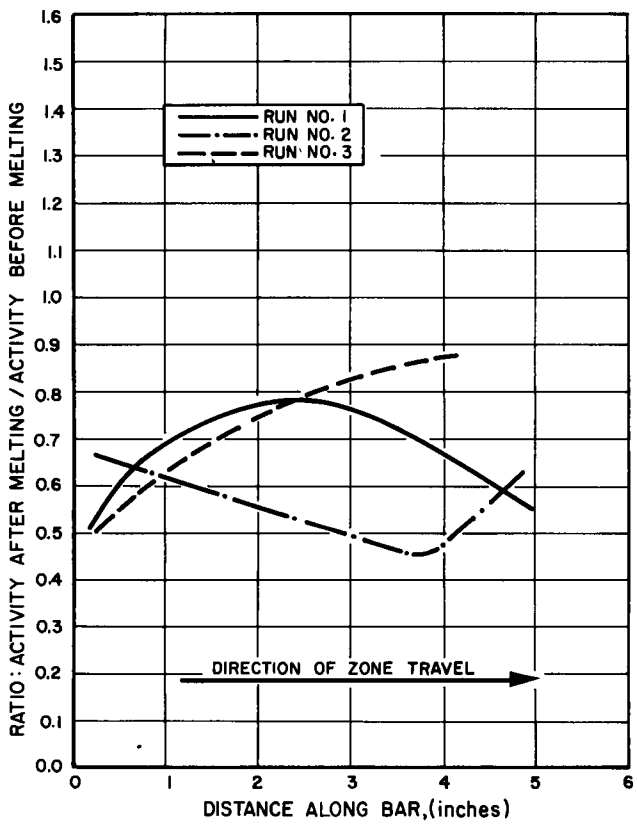

Fig 6. Cerium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy

3. Cerium (Fig. 6) - The data give no consistent results concerning cerium migration. Cerium was found in the volatilized material deposited on the hearth. Volatilization occurred because of the relatively high vapor pressure of cerium. The shapes of the curves can probably be associated with changing temperatures in the zone and changes in the size of the molten zone as it pro-

gressed through the specimen. These changing conditions might have caused local variations in the amount of volatilized cerium, the part remaining in the bar being distributed as shown in the figure. Run II is lower in cerium concentration than Run I because Run II had more time for volatilization. Run II indicates more cerium than Run II because the original concentration was higher.

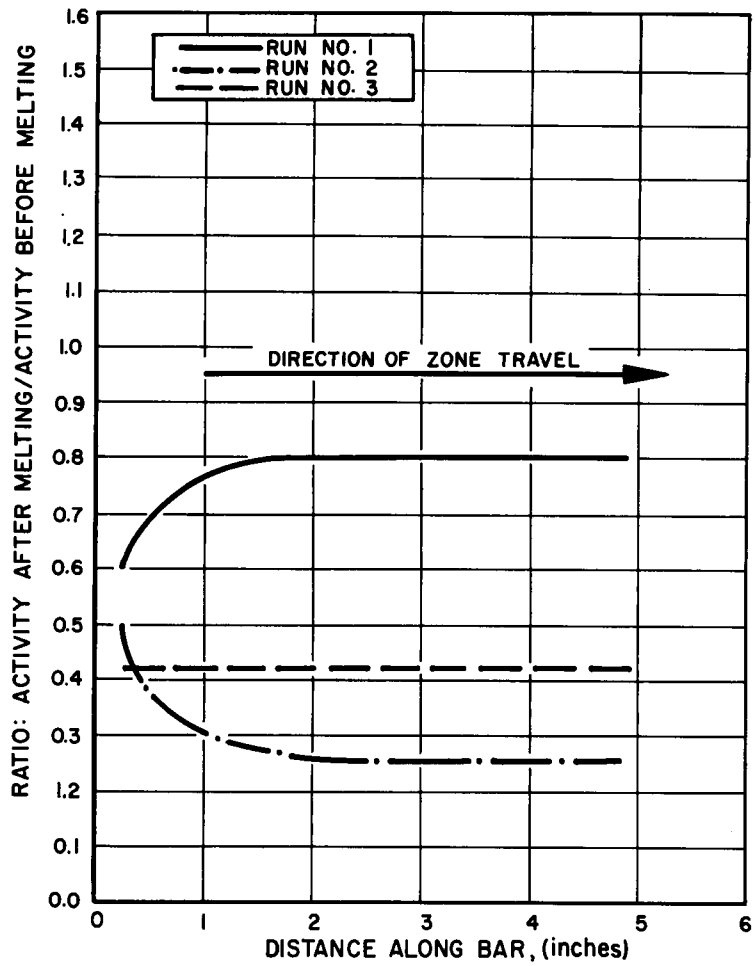

Fig. 7. Yttrium and Rare Earths Distribution in Zone Melted Irradiated Thorium-Uranium Alloy

4. Yttrium and Rare Earths (Fig. 7) - The shape of these curves results mostly from volatilization. Migration by zone melting might have an effect but it is not apparent. As in the case of cerium, Run II contains less yttrium and rare earths than Run I because of the greater duration of the molten state. Run III has more than Run II because the specimen originally contained more. Volatilization occurred, as is evidenced by the remaining concentration being less than the control, and yttrium plus rare earths were found in the material swabbed from the hearth.

5. Tellurium (Fig. 8) - This element shows the combined effects of zone melting and volatilization. Run I was too rapid for zone melting to be effective. The low concentrations relative to the control indicate volatilization. Run II displays an end region typical of zone melting in that the solute was carried along with the liquid and is found in the last zone, leaving it with the high concentration

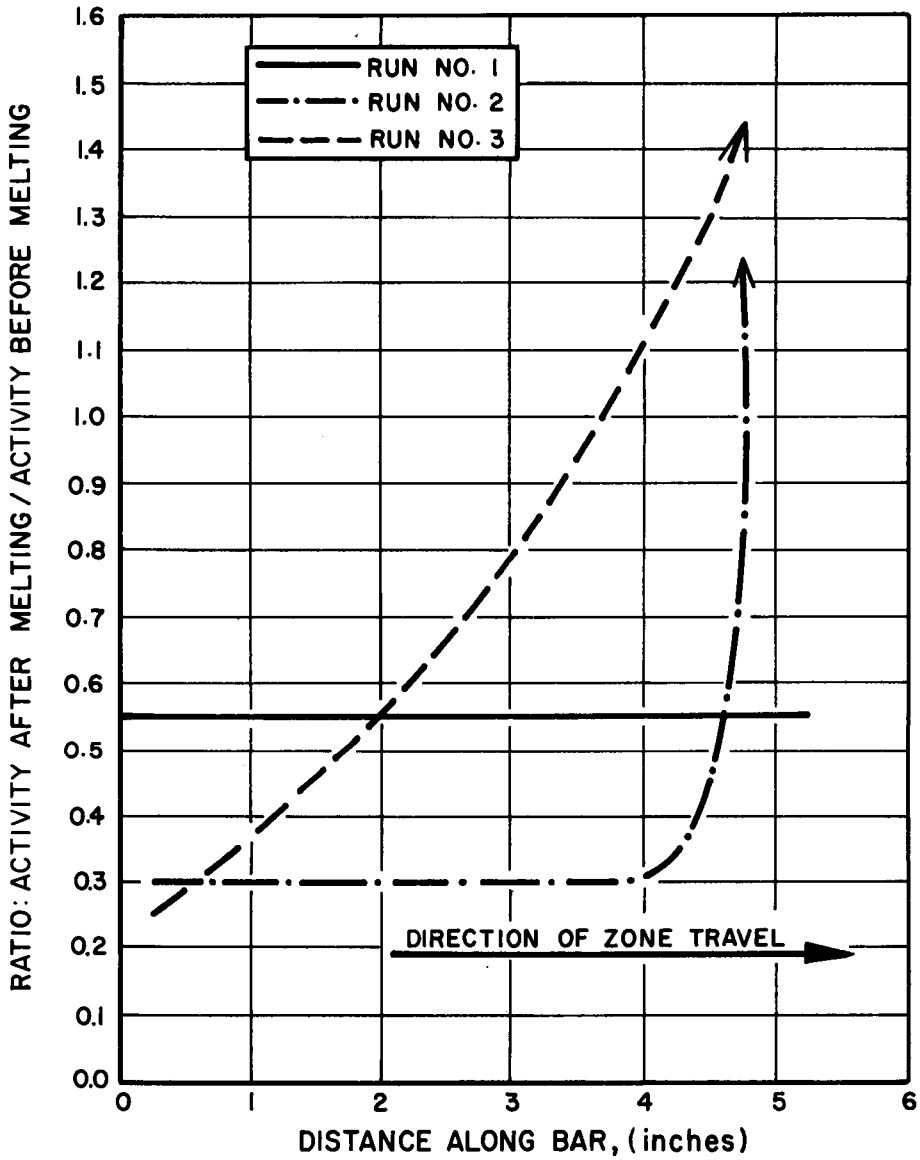

Fig. 8. Tellurium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy

shown. Run III had a higher original fission-product content but volatilization was not great enough or erratic enough to interfere with zone migration, hence, the resulting and typical curve shape.

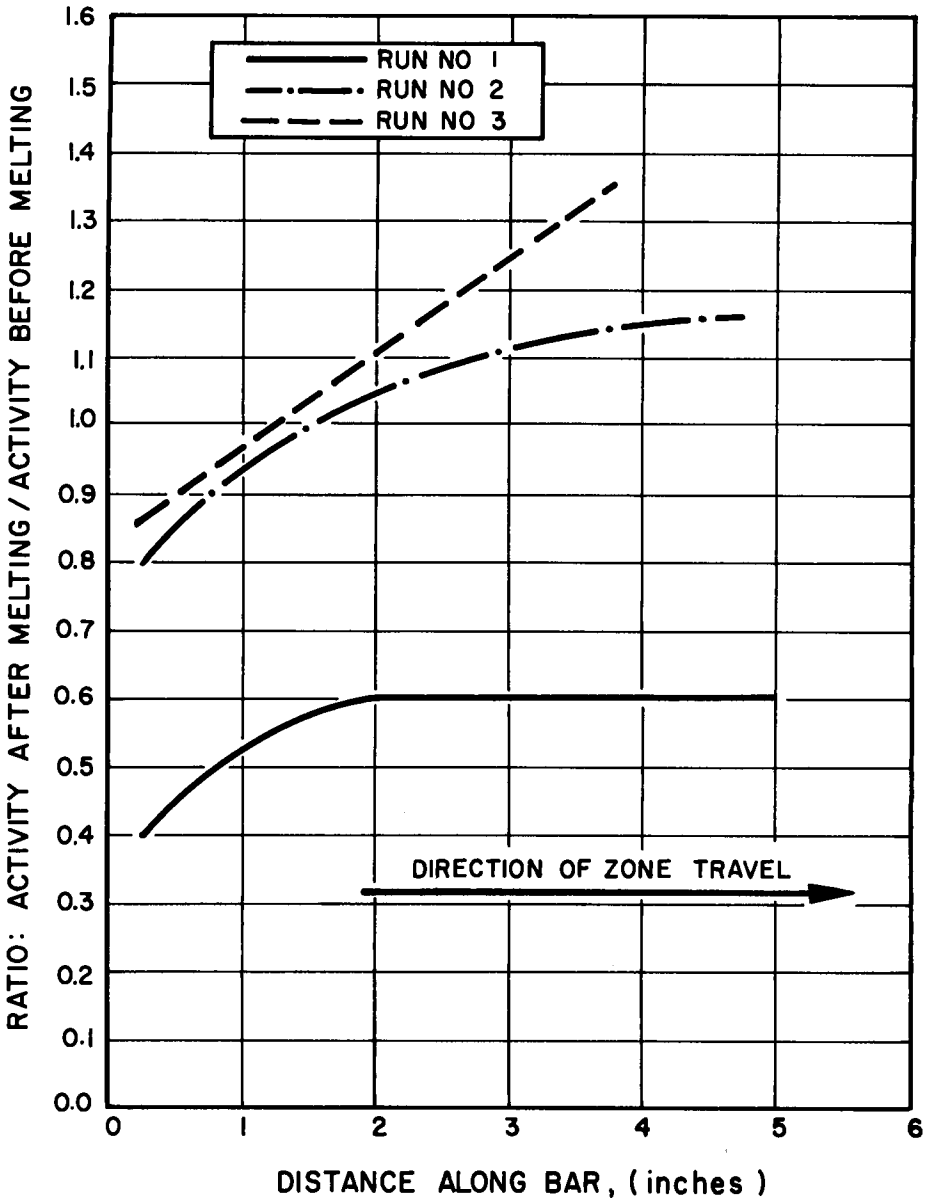

Fig. 9. Zirconium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy

6. Zirconium (Fig. 9) - The curves for runs II and III indicate zirconium migration in the direction of zone travel. These results are similar to those obtained in earlier zone melting experiments on thorium-zirconium alloys.[13] According to the constitutional diagram[16] for the thorium-zirconium system, zirconium separations should be obtained in the low zirconium region. Run I indicates a rather low concentration, which could be due to analytical error, since it has been demonstrated that loss by volatilization should not occur.[17]

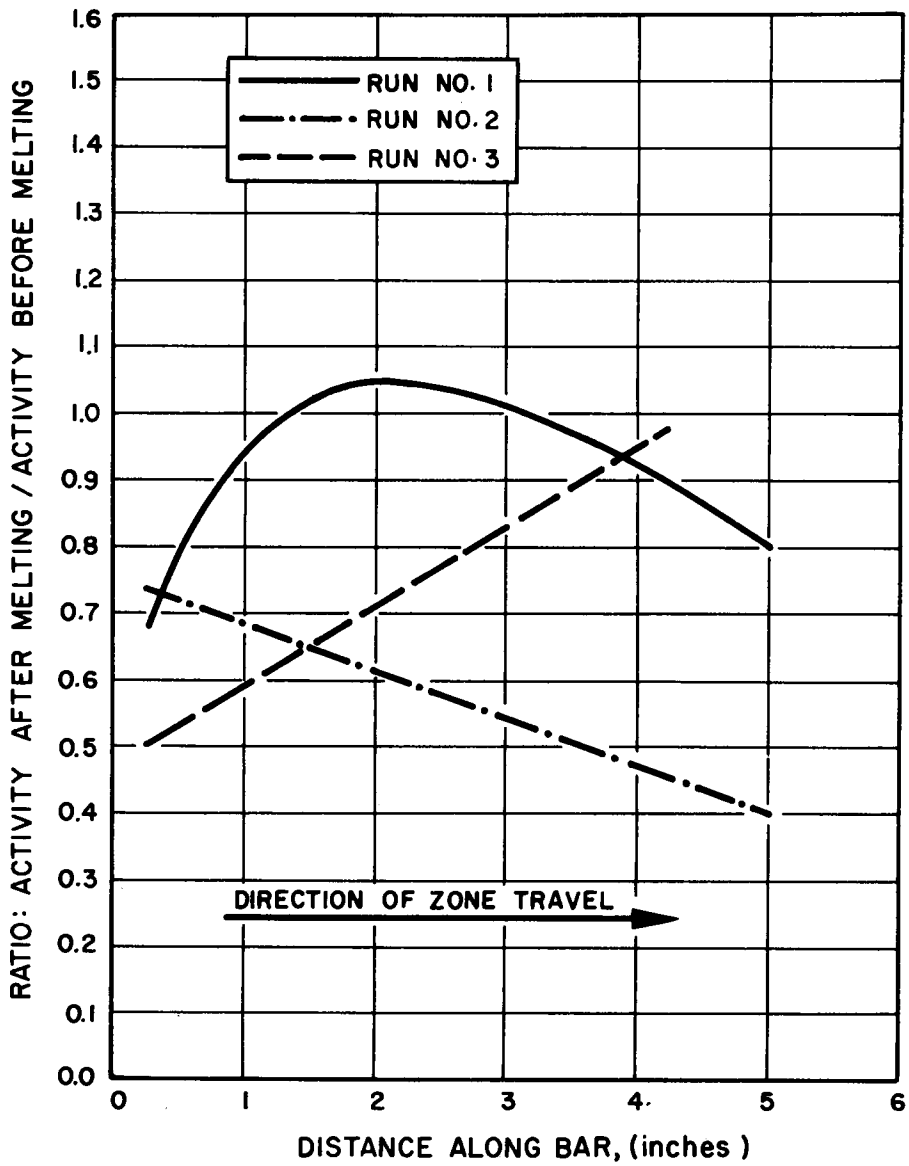

Fig. 10. Protactinium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy

7. Protactinium (Fig. 10) - The movement of this element presents a confusing picture, as no uniform trend is indicated. Run III looks typical, but confidence in it is destroyed by the shape of the other curves. The vapor pressure of protactinium is rather low, so volatilization would not be expected. However, all the curves indicate a loss of material. This might be an error in analysis because, if protactinium formed a complex which volatilized, this should be found in the volatilized material whereas none was observed. The three runs should show similar volatilization histories which would cause the curves to be similar or at least show a relative trend.

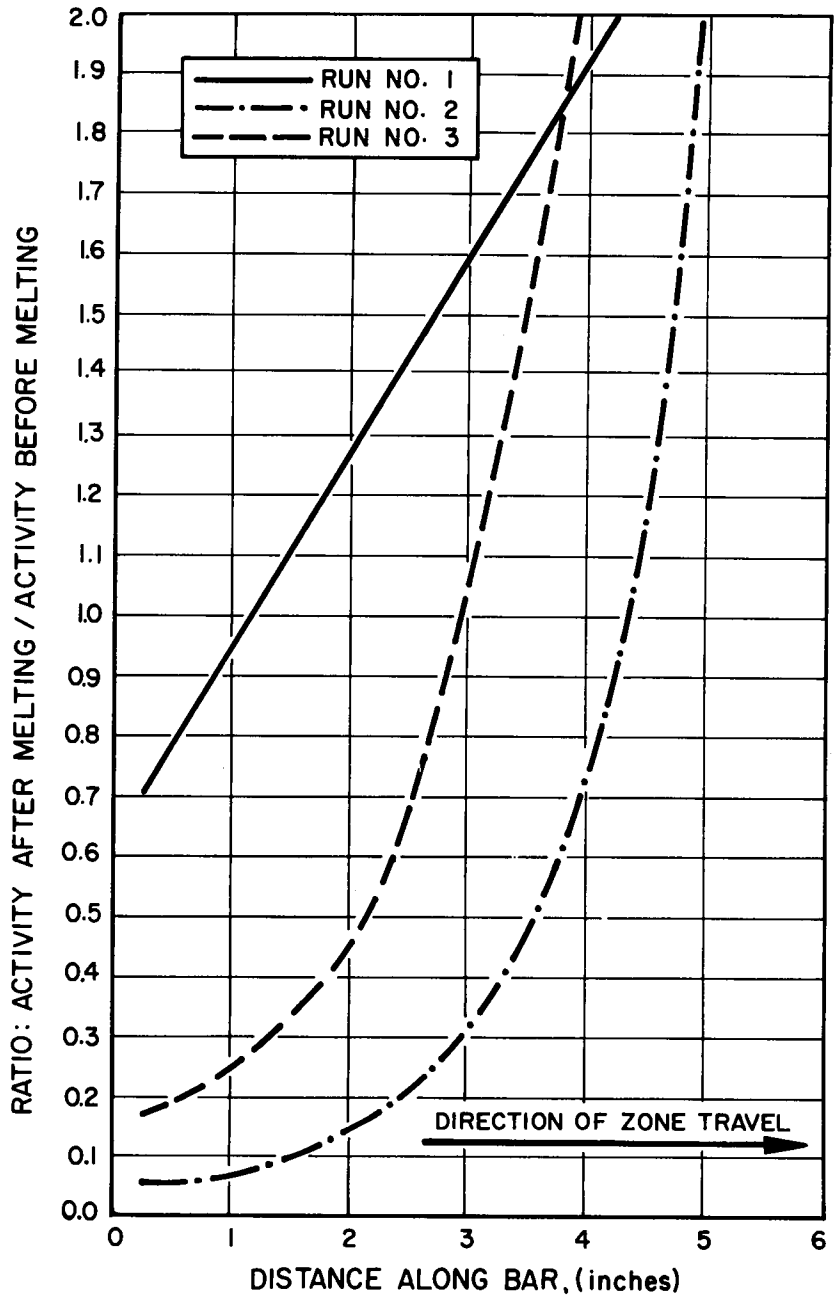

Fig. 11. Ruthenium Distribution in Zone Melted Irradiated Thorium-Uranium Alloy

8. Ruthenium (Fig. 11) - This element did not volatilize; therefore, its favorable concentration change is probably due to zone melting. Run I indicates a surprising migration in the zone direction, considering the rapidity of the passes. Run II shows better separation because it was slower. Run III indicates excellent separation, considering its greater original concentration.

B. DISCUSSION

The elements cesium and strontium are completely removed by volatilization. Redistribution of cerium, yttrium, and rare earths suggests a dual process of volatilization and zone melting with removal by volatilization being the dominant factor. Protactinium presents a confusing picture and more work is required to establish the effect of zone melting on this element.

Uranium, tellurium, zirconium, and ruthenium are successfully moved in the zone direction. In an attempt to emphasize the favorable zone melting

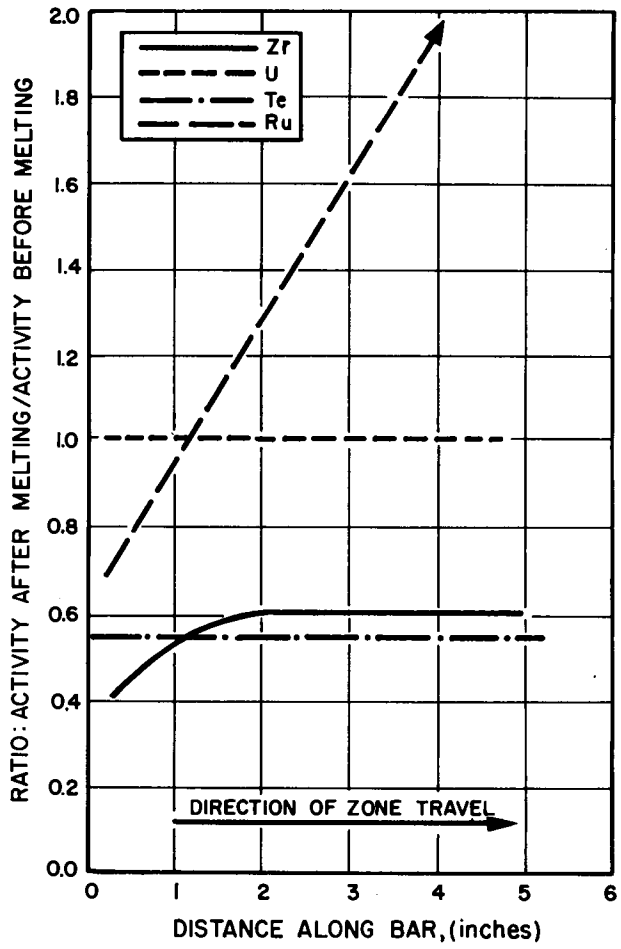

Fig. 12. Redistribution of Four Elements in Bar I

results of these four fission products their redistribution curves are regraphed in Fig. 12 through 14 according to each of the three specimen bars to which they belong.

Theoretical expectations of the effect of zone rates is encouragingly verified by the relative separations obtained for Bar I (Fig. 12) and Bar II (Fig. 13).

The two bars were purposely prepared, processed and analyzed similarly, the zone travel rate being the variable. Bar II, the slower of the two, shows improved purification compared to Bar I.

Bar II and Bar III (Fig. 14) have similar histories and zone rates, the principal variation being their initial uranium concentration and resultant fission product concentration. Bar II had 3 w/o uranium and Bar III had 16 w/o uranium. Bar III had a smaller diameter than Bar II but the authors and others believe this should have a negligible effect on the results. Again, as would be predicted by zone melting theory, the most effective purification occurred in Bar II because it contained less solute than Bar III.

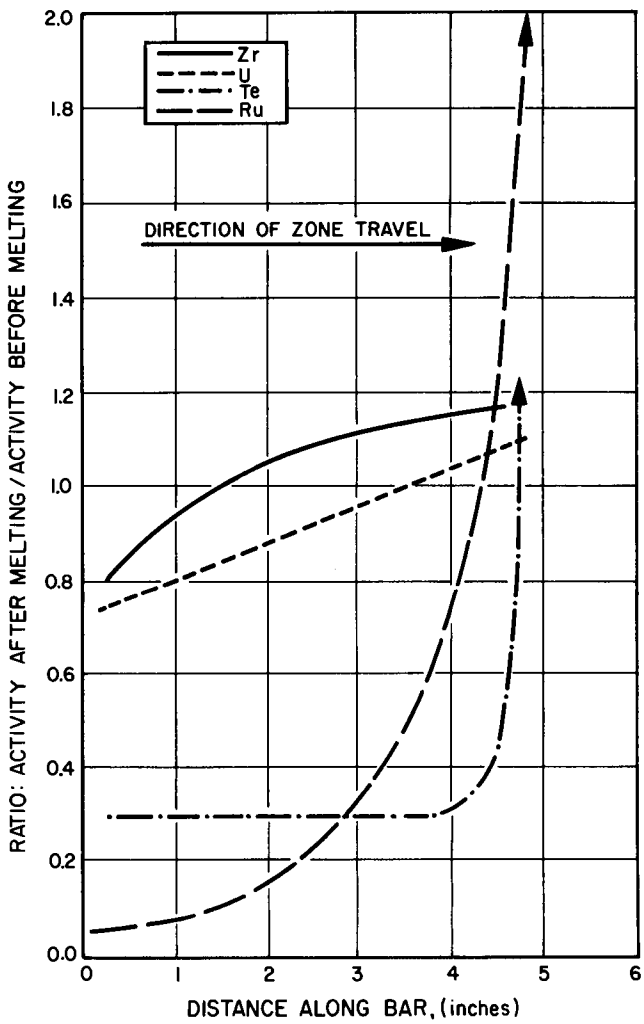

Fig. 13. Redistribution of Four Elements in Bar II

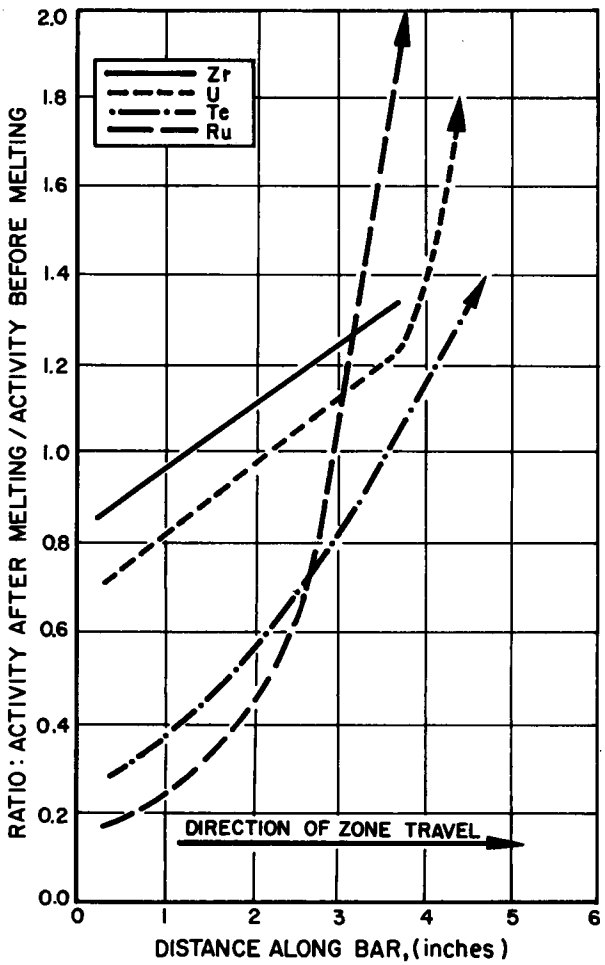

Fig. 14. Redistribution of Four Elements in Bar III

IV. CONCLUSIONS

The technical problems associated with a laboratory-scale removal of fission products by zone melting have been overcome. Results indicate that purification is obtained. Uranium, tellurium, zirconium, and ruthenium are successfully moved in the zone direction. Tellurium and ruthenium are moved to the end zones efficiently and it is possible to recommend this method for consideration as a removal process for these two elements. Cesium and strontium are completely removed by volatilization. Cerium, yttrium, and rare earths are removed by volatilization with various efficiencies, depending on the temperature and time fluctuations in the molten zone. Protactinium presents a confusing picture (Fig. 10) and more work is required to establish the effect of zone melting on this element.

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