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ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.

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DECONTAMINATION OF THORIUM-URANIUM ALLOY BY NONCONSUMABLE ELECTRODE ARC-MELTING

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ABSTRACT

The evaporation of fission products from thorium-uranium alloy by melting in an electric arc has been investigated. Effective removal of cesium and strontium was observed while the rare earths were partially removed and the refractory metals remained in the alloy. Uranium and protactinium are vaporized when heated at high temperatures and for long periods.

There is an indication that a consumable melting process is reasonably suitable as a high temperature method for decontaminating thorium fuels.

I. INTRODUCTION

The utilization of thorium as a fertile material for nuclear power reactors is now an accepted concept. Eventually there should be substantial quantities of spent thorium and thorium-uranium alloy fuels requiring reprocessing. As is the case with uranium fuels, high temperature methods, including evaporation, have been suggested as offering promise as an economical process for the decontamination of such fuels.

Of the high temperature methods, direct volatilization of contaminants from molten thorium is of interest as thorium and thorium-rich alloys melt at temperatures greater than 1600° C. Vapor pressures of some representative fission product elements, and of thorium, uranium, and protactinium at a temperature slightly above the melting point of thorium are listed in Table I. These values indicate that reasonable evaporation of cesium, tellurium, strontium, cerium, and the rare earths can be expected at 2000° K. Uranium, zirconium, thorium, protactinium, and ruthenium should not evaporate appreciably at this temperature.

TABLE I

VAPOR PRESSURE
OF REPRESENTATIVE ELEMENTS AT 2000° K [2]

Element	Vapor Pressure in 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	$< 10^{-6}$

One difficulty associated with experiments on molten thorium is containment. Molten thorium reacts with all the common refractories and alloys with the metals normally used in high temperature application.

A method which eliminates the containment problem is to melt the metal in the electric arc. The process consists of melting the thorium between a water cooled tungsten electrode and a water cooled copper hearth. The surface in contact with the cold copper hearth is chilled so that the metal is contained in a crucible of the same metal. The surface tension of most liquid metals is sufficiently high so that small samples form into buttons.

The electric arc is capable of producing quite high temperatures. Consequently, arc melting seems an ideal method for studying the volatilization of other elements from thorium.

The present investigation was made in order to study the decontamination of thorium-uranium alloy by the arc melting process and to correlate the results with existing vapor pressure data.

II. EXPERIMENTAL METHOD

A photograph of the arc-melting furnace appears in Fig. 1. The position of the electrode is adjustable in both the vertical and horizontal planes. The various cooling, vacuum, inert gas, and power leads are connected to the furnace and can be seen in the photograph. The arc is made inside the Vycor envelope so that an inert atmosphere can be maintained inside the furnace. The molybdenum electrode is tipped with tungsten. This technique was used to prevent water from leaking into the system as the tungsten used was slightly porous.

The vacuum pump is vented through a filter system for containment of volatile fission products. The arc is powered by a 300 ampere P & H direct current arc welder, Model No. 302. The welder has appropriate range selector switches so that the power input to the arc can be varied over a wide range.

In a typical experiment the piece of metal was placed on the hearth, the lid and electrode assembly were sealed in place, and the furnace evacuated. The system was flushed several times with helium by alternate filling and evacuation. Finally, the pressure was adjusted to one-half atmosphere of helium. The arc was then

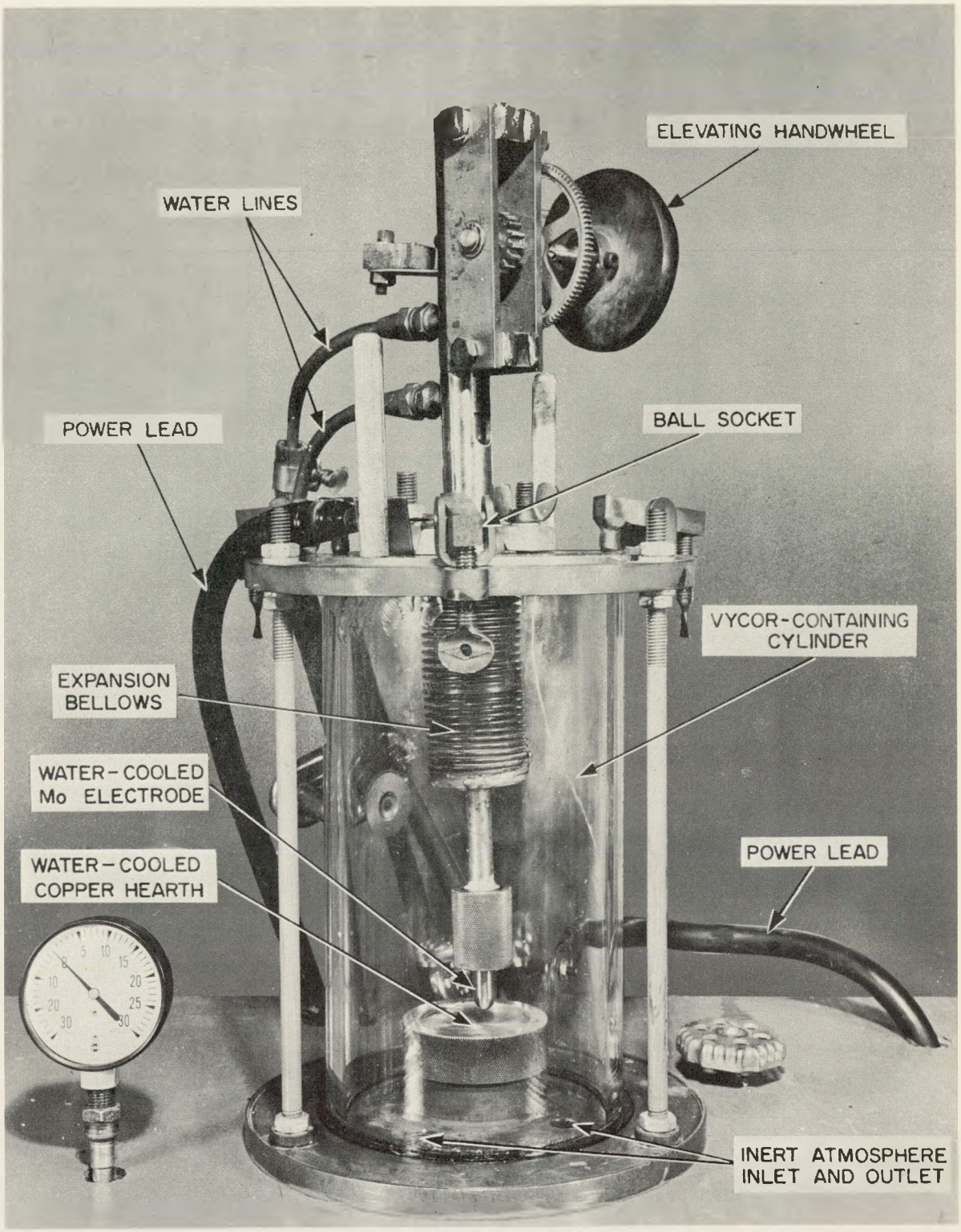

Fig. 1. Furnace for Nonconsumable Arc-Melting

struck and the button held in the molten state for the desired length of time. In most experiments, the amperage was varied between 10 and 50 amps. In the actual decontamination experiments, the button was heated on one side and then inverted to ensure that the entire piece of metal was melted during the run.

Between runs, the electrode and hearth were cleaned with steel wool to prevent cross contamination. After completion of the melt and allowing sufficient cooling time, the furance was opened to the atmosphere. The product button was then dissolved in concentrated nitric acid catalyzed by the addition of a small amount of fluoride ion. The resulting solution was then analyzed for fission products and in some cases thorium, uranium, and protactinium by standard analytical procedures.

Approximate temperatures were measured by sighting on the button surface with an optical pyrometer.

A series of runs was made to indicate the effects of time of heating and sample weight upon the decontamination results. This first group of experiments was carried out on thorium-3 w/o uranium alloy irradiated to a nvt* of 10^{17}. The last three melts in this series were made in the presence of calcium fluoride as a drossing agent.

A second series was made using thorium-10 w/o uranium alloy also irradiated to a nvt of 10^{17}. The variable studied was temperature.

Series 3 was carried out with slightly irradiated pure thorium (nvt = 10^{13}) to determine protactinium loss without interference from other fission products.

In group 4, unirradiated thorium-10 w/o uranium alloy samples were melted to determine thorium and uranium losses under severe heating conditions.

A fifth series was carried out using slightly irradiated (nvt = 10^{13}) thorium-3 w/o uranium alloy to determine thorium, uranium and protactinium losses on the same samples.

For each group of experiments a sample of metal with the same history as that used in the melts was dissolved and analyzed as a control.

Recorded temperatures may be in error by a hundred degrees since light from the arc plasma may interfere with the optical measurement, and the sight window

* nvt = integrated neutron flux

becomes coated during the course of a melt. Furthermore, a severe temperature gradient must exist across the button as the top surface is molten and the bottom surface solid. Consequently, the temperatures listed must be regarded merely as an indication of the relative temperature of each sample in each series.

The times listed in the subsequent tables are the total heating times for both sides of the button. Obviously, the entire button was not molten for the time listed as one surface is always nearly frozen. However, it is believed that the bulk of the sample is molten as in one experiment, the button actually rolled over while molten. This observation would indicate that only a small layer of the sample is in the solid state. Also, the arc tends to "hunt" during a melt so that the physical shape of the button varies during its molten period. Therefore, it is believed that listing the total melting time gives the best approximation of the actual case.

III. RESULTS AND DISCUSSION

Due to the uncertainty in measured temperatures and the unknown area-to-weight ratio of the sample, correlations of the type previously reported by Cubbiciotti[3] and Milne[1] are not possible. Consequently, the results must be discussed more from a qualitative than quantitative standpoint.

The data obtained in initial work are presented in Table II.

In general the decontamination results follow the trend predicted from the vapor pressure data. Strontium and cesium are effectively removed; cerium and rare earths are partially removed while the more refractory metals such as zirconium are not removed. The tellurium results are anomalous as the amount removed varied in no predictable fashion. This may be the result of telluride formation. In those runs where protactinium analyses were made, more removal was noted that would be expected from the vapor pressure data. However, the data listed in Table I are only approximate.

Although careful evaluation of evaporation as a function of heating period and sample weight was not carried out, the data indicate that longer molten periods increase evaporation of fission products. On the other hand, increased sample weights, i.e. size, tends to decrease evaporation.

TABLE II

RESULTS ON IRRADIATED Th-3 w/o U ALLOY

Run No.	Time (min)	Weight (gm)	Temp. (°C)	Per Cent Fission Produce Removed							
				Ce	R.E.	Cs	Sr	Te	Zr	Pa	Ru
2	32	2.85	1650	25	52	99	100	20	0	-	1
4	42	4.10	1800	35	65	99	100	73	0	-	1
5	24	2.51	1850	85	78	95	99	89	0	31	0
6	20	2.61	1850	-	-	99	99	96	0	25	0
8*	16	2.32	1860	66	89	80	92	55	0	-	0
9*	16	2.43	1800	74	87	88	93	52	0	-	0
10*	16	2.68	1850	80	94	82	94	45	12	-	0

* These melts were made in the presence of 0.1 gm of CaF_2 as a drossing agent.

In the three runs made in the presence of calcium fluoride, rare earth removal was slightly enhanced while the evaporation of strontium and cesium was suppressed. No immediate explanation of these results is obvious.

The results of Series 2 listed in Table III are quite similar to those of the first group.

TABLE III

RESULTS ON IRRADIATED Th-10 w/o U ALLOY

Run No.	Time (min)	Weight (gm)	Temp. (°C)	Per Cent Fission Product Removed							
				Ce	R.E.	Sr	Zr	Pa	Ru	Nb	U
11	2	2.80	1900	64	78	98	0	8	0	0	6
12	4	2.89	1900	31	53	98	0	-	0	0	5
13	8	2.23	2000	95	58	99	16	49	0	trace	10
14	8	3.06	2000	53	73	99	-	49	0	trace	3

Partial removal of cerium and rare earths and essentially complete removal of strontium was noted. In this series, uranium analyses were also carried out.

The results on uranium loss corroborate the rare earth data in that the removals of these materials are parallel. For example, run 13 showed 10 per cent removal of uranium and very high removals of the rare earths. Run 14 was intended to be under the same conditions as run 13, but the evaporation of uranium and rare earths was much less. This result also illustrates the uncertainty in the temperature measurement.

Interpretation of the data summarized in Table III cannot be precise, but it is indicated that increasing the temperature results in larger fractions of evaporated fission products.

Series 3 was run primarily to determine the protactinium loss more accurately. As Pa^{233} is the precursor of the fissionable isotope U^{233}, it is desirable to keep protactinium loss at a low level.

Protactinium losses obtained from the third series are listed in Table IV.

TABLE IV

RESULTS ON IRRADIATED THORIUM – PURE

Run No.	Time (min)	Weight (gm)	Temp. (°C)	Per Cent Removed (Pa)
15	4	3.29	1950	4.3
16	8	3.64	1950	41
17	8	4.17	1900	30
18	10	4.20	1700	7.5

These data disclose that protactinium can be partially evaporated at the temperatures obtained in the arc. The runs at high temperature for longer periods show significant protactinium loss.

The results from Series 4 are presented in Table V.

The times and temperatures for these experiments were longer and higher than in the previous series. Using 10 w/o uranium alloy and severe heating conditions loss of uranium is readily detectable. The results show that significant uranium losses result from excessive heating of the metal.

TABLE V

RESULTS ON UNIRRADIATED Th-10 w/o U ALLOY

Run No.	Time (min)	Weight (gm)	Temp. (°C)	Per Cent Removed	
				(Th)	(U)
19	10	2.98	1900	0.93	3.5
20	30	4.37	1900	3.4	8.4
21	20	5.58	2000	8.8	20.0
22	10	7.50	1950	3.7	6.8

The results obtained in Series 5 are presented in Table VI.

The results correlate reasonably well with those obtained in the previous series. Run 26 showed a 95 per cent removal of protactinium which seems high in comparison with previous results.

TABLE VI

RESULTS ON SLIGHTLY IRRADIATED Th-3 w/o U ALLOY

Run No.	Time (min)	Weight (gm)	Temp. (°C)	Per Cent Removed		
				(Pa)	(U)	(Th)
23	5	2.35	1900	23	3.53	0.68
24	20	2.99	1900	37	17.29	3.16
25	10	3.97	2000	28	10.45	3.04
26	5	4.11	2100	95	13.63	2.43
27	30	4.82	1800	78	0.74	0.70

It is of interest to compare the results obtained in this investigation with those obtained by direct volatilization from crucible contained material as done by Milne.[1] In general, the two sets of data agree reasonably well. The present work shows essentially no loss of the refractory metals such as ruthenium.

One other result can be inferred from these data, namely the relative volatility of uranium and thorium. The reported vapor pressures[2] yield a vapor pressure ratio of 20 for uranium and thorium, whereas the percentage removal data in

Table VI give a value of 3 to 6 for this ratio. This result indicates that the reported vapor pressure of thorium is incorrect.

IV. ENGINEERING FEASIBILITY

The research reported herein was undertaken as a preliminary effort designed to permit cursory evaluation of fission product evaporation from irradiated thorium-uranium alloy which had been nonconsumably arc melted. From an engineering standpoint consumable electrode arc melting offers more promise. Consumable electrode melting is best carried out in an evacuated furnace, whereas in non-consumable melting the arc is more stable when operated in a mixed helium, argon atmosphere. Thus, the vacuum required for consumable melting enhances evaporation of impurities from the molten metal. Consumable melting permits better temperature control as well as more facile remote handling operation and maintenance of the arc furnace. Studying Beall's work on consumable electrode arc melting, one may infer that this technique could allow rough slug casting directly from the molten alloy.[4] No major loss of metal will occur as the frozen skull resulting from the tilt pouring procedure may be reprocessed or even allowed to remain in the water cooled copper crucible hearth. In summary, it is suggested that the reported decontamination values, obtained by non-consumable melting, indicated that the more easily engineered consumable process, when remotely operated and maintained, may provide a direct method for decontamination and recasting of thorium-uranium reactor fuels.

V. CONCLUSIONS

The results of these experiments show that appreciable decontamination of irradiated thorium-uranium alloy can be effected by arc-melting. The rare gases and the more volatile elements are effectively removed. The rare earths are partially removed and the more refractory metals are not evaporated. These results are those which would be expected after considering vapor pressure data.

The results reveal that uranium and protactinium can be lost by excessive heating.

These data yield a value of 3 to 6 for the ratio of the vapor pressures of uranium and thorium.

It is suggested that consumable arc melting might offer greater decontamination and better operational control than non-consumable arc melting. It would also be an easier process to engineer.

REFERENCES

1. T. A. Milne and C. T. Young, NAA-SR-1680, December 15, 1956.
2. L. L. Quill, The Chemistry and Metallurgy of Miscellaneous Materials, McGraw Hill, New York, 1950, p 28-31.
3. D. Cubicciotti, NAA-SR-242, April 30, 1953.
4. R. A. Beall, J. O. Borg, and F. W. Wood, RI-5144, August 1955.