APPROVED FOR PULBIC RELEASE

[redacted]

UNCLASSIFIED

CIC-14 REPORT COLLECTION
REPRODUCTION
COPY

LA-2132
Copy No. C.3

AEC RESEARCH AND DEVELOPMENT REPORT

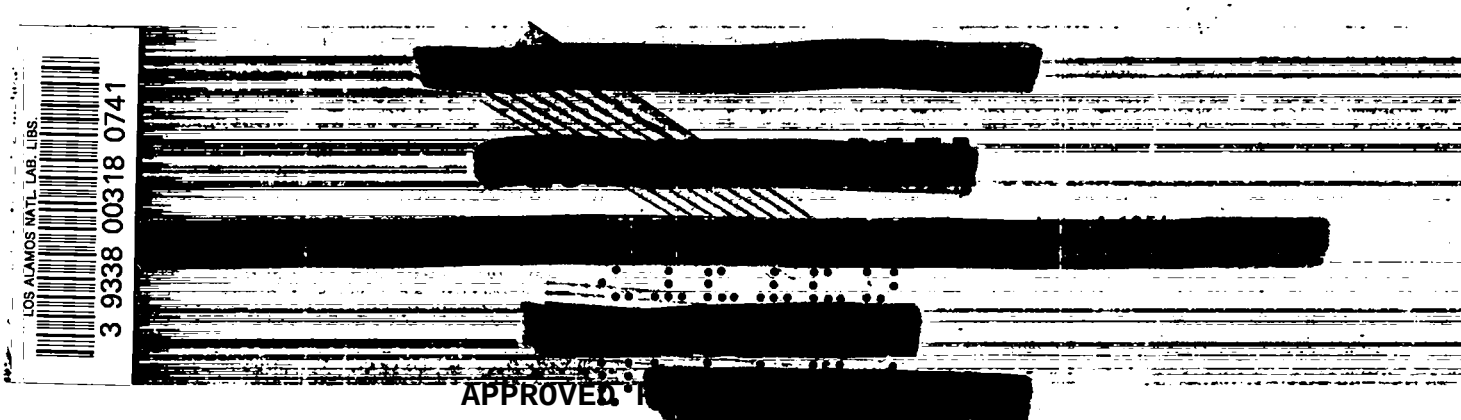
LOS ALAMOS SCIENTIFIC LABORATORY

OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

PYROMETALLURGY EXPERIMENTS ON PLUTONIUM-RICH REACTOR FUELS

(Project Status Report as of March 31, 1957)

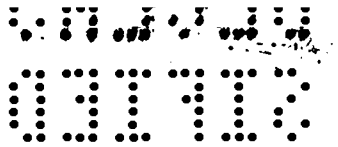
UNCLASSIFIED



LOS ALAMOS NATL. LAB. LIBS.
3 9338 00318 0741

APPROVED [redacted]

APPROVED FOR PULBIC RELEASE



LEGAL NOTICE

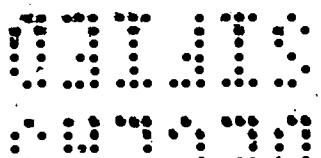
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission..

Printed in USA. Charge 35 cents. Available from the U. S. Atomic Energy Commission, Technical Information Service Extension, P. O. Box 1001, Oak Ridge, Tennessee. Please direct to the same address inquiries covering the procurement of other classified AEC reports.



APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

PUBLICLY RELEASABLE
LANL Classification Group
B. Folsom
9/8/95

UNCLASSIFIED

LA-2132
C-16, CHEMISTRY--TRANSURANIC ELEMENTS
(M-3679, 20th ed.)

This document consists of 29 pages
No. [redacted] of 197 copies, Series A

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

REPORT WRITTEN: May 8, 1957

REPORT DISTRIBUTED: September 16, 1957

[redacted] to OFFICIAL USE ONLY
by authority of [redacted] Atomic [redacted]
Per [redacted]
By REPORT LIBRARY
12-30-57
1-2-58

PYROMETALLURGY EXPERIMENTS ON PLUTONIUM-RICH REACTOR FUELS

(Project Status Report as of March 31, 1957)

Classification changed to UNCLASSIFIED
by authority of the U. S. Atomic Energy Commission,
Per W. J. Carroll - 7/20/59
By REPORT LIBRARY M. Plack
JUL 24 1959

Work done by:
J. A. Leary
W. J. Maraman
R. Benz

Report written by:
J. A. Leary

Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

UNCLASSIFIED

[redacted]

LOS ALAMOS NATIONAL LABORATORY
3 9338 00318 0741

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

UNCLASSIFIED

[redacted]

UNCLASSIFIED

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]SIFIED [redacted]

UNCLASSIFIED

ABSTRACT

Experiments on the purification of plutonium-cobalt and plutonium-iron fuel alloys by pyrometallurgical methods are reported. Oxidative slagging appears to be an effective method for removing essentially all of the rare-earth fission product elements, whereas zirconium, molybdenum, and ruthenium concentrations are not seriously affected. Other methods, such as liquation, fluoride and carbide slagging, liquid metal extraction, and various fused salt systems are also being studied.

ACKNOWLEDGEMENTS

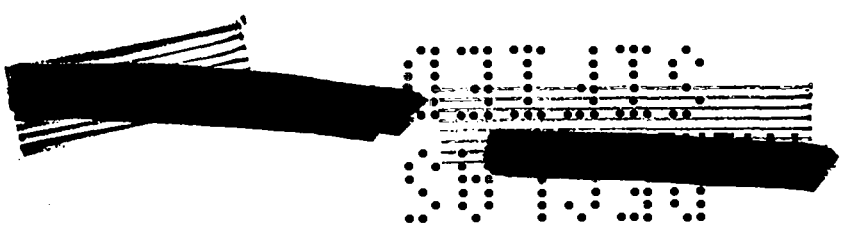
All chemical analyses were done by members of Group CMB-1 under the direction of C. F. Metz. Metallography was done by Group CMF-5 under the direction of A. S. Coffinberry. The advice of R. D. Baker on all phases of the project is also gratefully acknowledged.

UNCLASSIFIED

[redacted]SIFIED [redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE



APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

UNCLASSIFIED

FOREWORD

Although considerable work has been reported on the purification of uranium fuels by pyrometallurgical methods, a dearth of information on plutonium-rich fuel systems exists at the present time. However, there appears to be considerable interest in plutonium pyroprocessing methods. It is for this reason that the following status report of current exploratory experiments has been written, rather than waiting to report when various phases of the problem have been completed. Periodic status reports on this project will be published in the future.

UNCLASSIFIED

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

TABLE OF CONTENTS

		Page
ABSTRACT		3
ACKNOWLEDGEMENTS		3
FOREWORD		5
1.	INTRODUCTION	9
2.	EQUIPMENT	9
3.	PREPARATION OF ALLOYS	11
4.	LIQUATION EXPERIMENTS	16
5.	OXIDATIVE SLAGGING	19
6.	CARBIDE SLAGGING	27
7.	FLUORIDE SLAGGING	28
8.	FUTURE EXPERIMENTAL PROGRAM	28
9.	REFERENCES	29

LIST OF FIGURES

1.	VACUUM INDUCTION FURNACE	10
2.	VACUUM CASTING SET-UP	12
3.	MAGNESIA CRUCIBLE, TYPE A-392	18
4.	STANDARD FREE ENERGY OF FORMATION OF THE OXIDES OF SOME TYPICAL FISSION PRODUCT ELEMENTS	21

LIST OF TABLES

1.	COMPOSITION OF FISSIUM ALLOY CASTINGS	13
2.	MATERIAL BALANCE FOR ADDED FISSIUM ELEMENTS	14
3.	COMPOSITION OF IRON-FISSIUM ALLOY	15
4.	EFFECT OF LIQUATION ON THE COMPOSITION OF COBALT FISSIUM	17
5.	EFFECT OF LIQUATION ON THE COMPOSITION OF IRON FISSIUM	19
6.	EFFECT OF OXIDATIVE SLAGGING ON THE COMPOSITION OF COBALT FISSIUM	22

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

LIST OF TABLES (continued)

Page

7. EFFECT OF OXIDATIVE SLAGGING ON THE COMPOSITION OF IRON FISSIUM 23
8. EFFECT OF TIME AND TEMPERATURE ON RARE-EARTH REMOVAL BY OXIDATIVE SLAGGING 24
9. EFFECT OF OXIDATIVE SLAGGING ON CONCENTRATIONS OF RADIOACTIVE FISSION PRODUCTS IN FISSIUM ALLOY (Experiment PIF-12). 26
10. SPECIFIC ACTIVITIES OF FISSION PRODUCT ELEMENTS BEFORE AND AFTER OXIDATIVE SLAGGING (Experiment PIF-12) 26
11. EFFECT OF CARBIDE SLAGGING ON THE COMPOSITION OF COBALT FISSIUM (Experiment PCF-8) 27
12. EFFECT OF FLUORIDE SLAGGING ON THE COMPOSITION OF COBALT FISSIUM 28

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

1. INTRODUCTION

In conjunction with the Los Alamos Molten Plutonium Reactor Experiment[1] (LAMPRE), a development program has been initiated to study pyrometallurgical methods of purifying spent plutonium fuel. The relative merits of high-temperature processing have been discussed previously[2-5] and will not be reviewed here. However, certain special features of the proposed LAMPRE fast reactor are pertinent to processing objectives. The loss in fuel reactivity due to dilution by fission products is approximately ten times the loss due to neutron capture by fission products. Moreover, because the fuel is used in liquid form, it is not necessary to eliminate a high gamma radiation level, as would be required for many cases of solid fuel element fabrication. Thus, the purification problem is essentially one of fission product bulk removal, with no stringent specification on any particular contaminant.

At the present time, pyrometallurgy experiments on plutonium-rich systems are being conducted on an 85-g. scale. When the exploratory phases are complete, potential unit operations will be evaluated at the 1-kg. scale. Until shielded facilities for handling high-burnup plutonium fuel are available, all experimental work is being conducted with the synthetic spent fuel, "fissium," similar to that used for uranium fuel systems at Iowa State College.[6]

2. EQUIPMENT

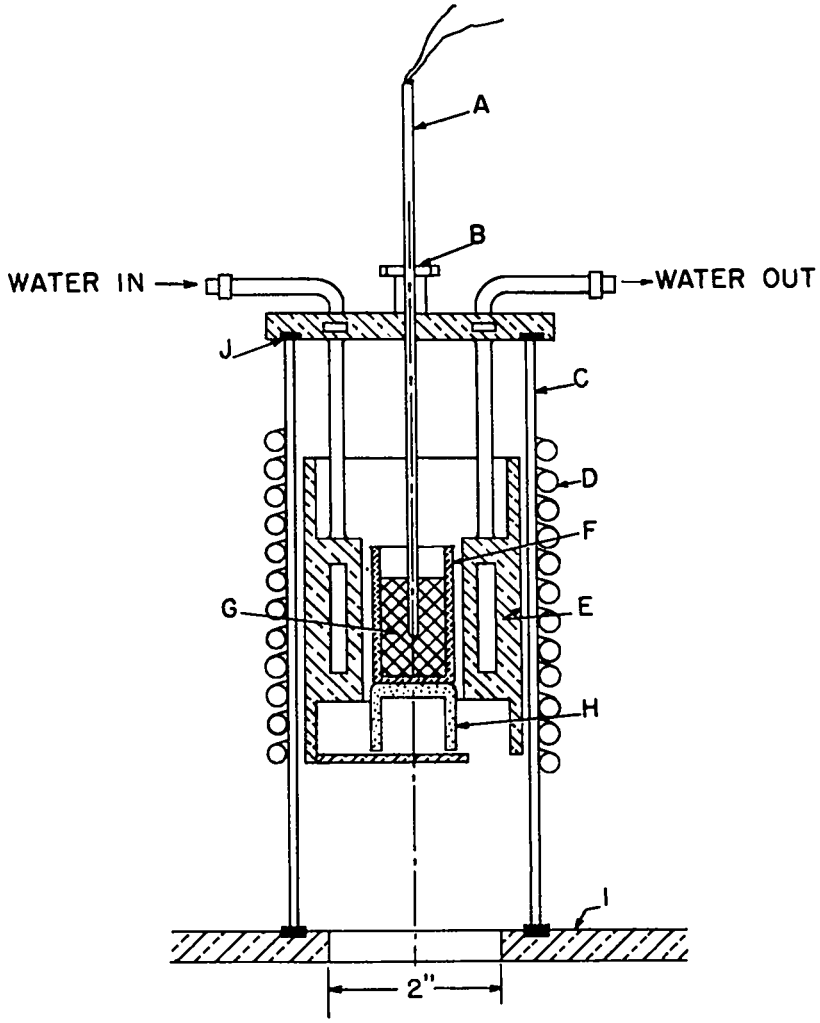
The vacuum induction furnace used for alloying, casting, and slagging is shown schematically in Fig. 1. Normally the melt was heated directly by means of a water-cooled current concentrator surrounding the ceramic crucible. In the alloying process, however, the melt was heated indirectly by the containing tantalum crucible. Energy was supplied to the current concentrator by an external water-cooled induction coil. A 3-KVA Ajax spark-gap converter was used to energize the coil. A 100 mm. diameter Pyrex tube with lubricated ground ends was used as the vacuum envelope surrounding the current concentrator. The top of the current concentrator also served as a vacuum wall, while the bottom of the current concentrator and the Pyrex tube were open to the vacuum can which was

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]



A Tantalum pyrometer tube
B Vacuum seal
C Pyrex vacuum envelope
D Water-cooled induction coil
E Water-cooled current concentrator
F Crucible
G Molten alloy
H Magnesia pedestal
I Top of vacuum can
J Neoprene flat gaskets

FIG. 1. VACUUM INDUCTION FURNACE

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

connected to an oil diffusion pump and forepump. The system was normally evacuated to a pressure of 0.04 μ before heating the crucible charge. During the heating, the pressure normally increased to about 1 μ. After the initial outgassing, it was possible to maintain a pressure of 0.05 μ while the crucible charge was at 1450°C.

The experimental arrangement for vacuum chill-casting the alloy is shown in Fig. 2. Before assembly, a magnesia stopper rod was hand-lapped to seat in a 3/8 in. diameter hole in the bottom of the pouring crucible. When the melt reached a temperature of 1000°C. (normally within 15 min.), the stopper rod was raised about 1/4 in. by withdrawing the extension rod, and the melt flowed into the chill-casting mold. The mold was made by bolting together two copper plates (each 6 in. wide, 9 in. high and 3/4 in. thick) and drilling two 5/8 in. diameter blind holes parallel to the longest dimension and centered at the joining plane. After cooling, this split mold was disassembled by removing the bolts and two cylindrical rods of alloy were recovered. The smooth bright surfaces of the rods indicated that the mold had been completely filled, and that there had been no reaction between alloy and mold.

3. PREPARATION OF ALLOYS

It was planned initially to use plutonium - 12 atomic per cent cobalt alloy (m. p. 405°C.) as the reactor fuel. Although the fuel composition was eventually changed, pyrometallurgical experiments were conducted before this alloy was found to be undesirable for metallurgical reasons. The results of these experiments will be reported for comparison with results obtained later using plutonium-iron alloy.

Preparation of Plutonium - 12 Atomic Per Cent Cobalt Alloy

One kg. of alloy was made by comelting plutonium with 3.25 weight per cent (w/o) cobalt in a tantalum crucible. The melt was heated in the vacuum induction furnace and held at 1200°C. for 2 hr. After cooling, the crucible was removed and the ingot was sampled for chemical analysis. All sampling was done by machining in an enclosed lathe box provided with an inert atmosphere. The average chemical analysis was 3.24 ± 0.02 w/o cobalt. Tantalum content of the ingot was 0.01 w/o.

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

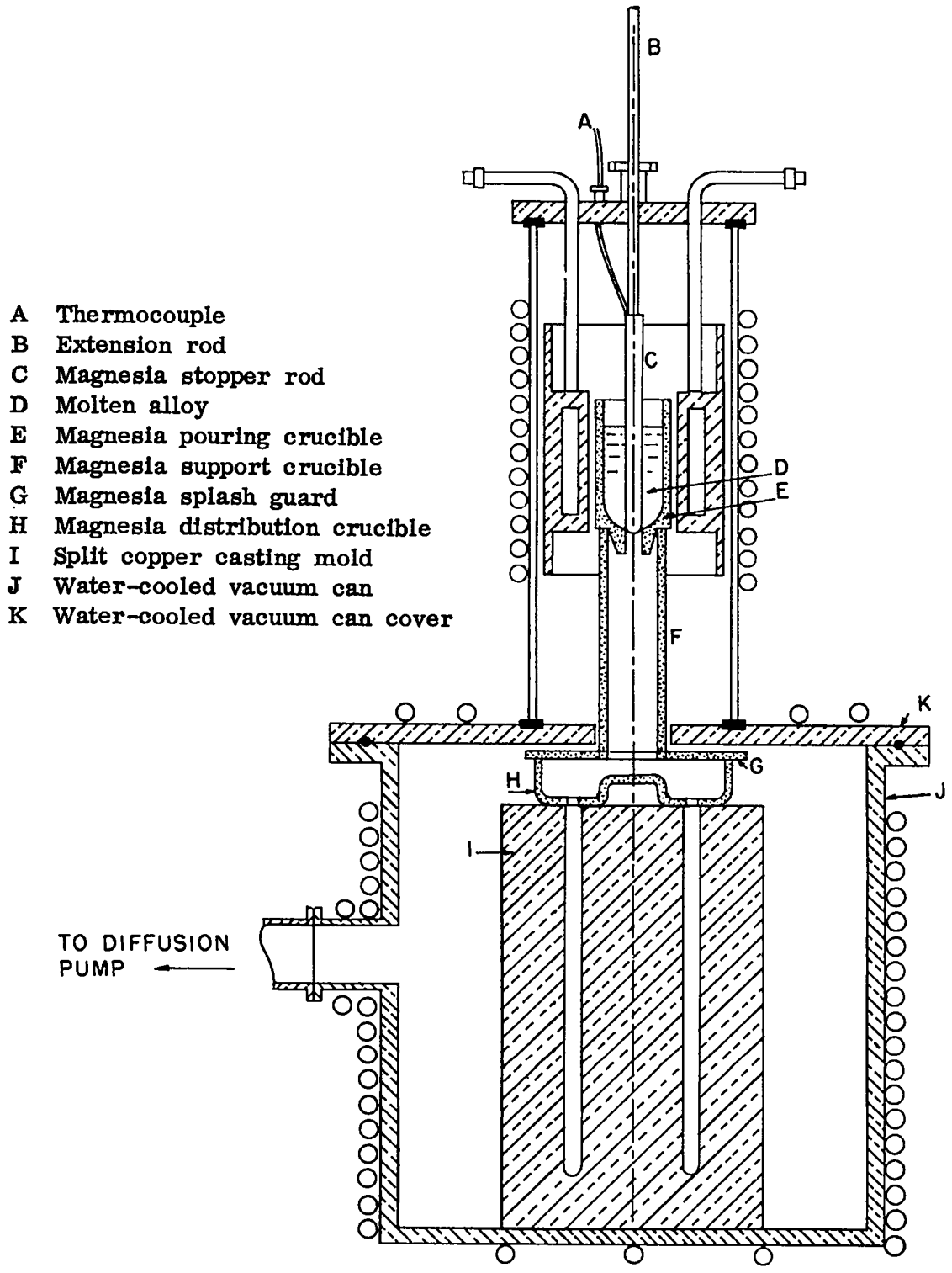


Fig. 2. VACUUM CASTING SET-UP

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

Preparation of Cobalt-Fissium Alloy

Representative fission product elements were added to the cobalt alloy to approximate a "once-through" 10 per cent fuel burnup, and the mixture was held at 1000°C. for 4 hr. in a vacuum induction furnace. (It was planned to add an additional amount of rare earths when the metals became available, but the change to plutonium-iron alloy was made before this could be done.) A thermal arrest was obtained at 410°C. on cooling. This alloy was then transferred to a magnesia bottom-pouring crucible, heated to 1000°C. and chill-cast into two 5/8 in. diameter cylindrical rods. The top, center, and bottom section of each rod was sampled, and the rods were cut into 1 in. lengths weighing approximately 85 g. each.

Chemical analyses of the samples are reported in Table 1.

Table 1

COMPOSITION OF FISSIUM ALLOY CASTINGS

Sample	Concentration of Element, w/o					
	Zr	Mo	Ru	Ce	Co	Ta
Rod No. 1 - Top	0.58	0.34	0.99	0.64	3.49	0.03
Center	0.57	0.35	0.98	0.62	3.55	0.03
Bottom	0.55	0.28	0.91	0.61	3.49	0.03
Rod No. 2 - Top	0.62	0.37	0.91	0.61	3.63	0.03
Center	0.62	0.32	0.94	0.64	3.37	0.03
Bottom	0.51	0.31	0.93	0.61	3.70	0.03
Over-all average	0.58	0.33	0.94	0.62	3.54	0.03
"As-added" composition	0.899	0.765	1.075	0.816	3.47	0

Because the concentrations of added elements were in general lower than the added amounts, the skull from the pouring crucible was dissolved completely and analyzed chemically. A material balance of added elements is shown in Table 2.

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

Table 2

MATERIAL BALANCE FOR ADDED FISSIUM ELEMENTS

Location	Amount of Element Present, g.				
	Zr	Mo	Ru	Ce	Co
In oxide skull	3.6	4.3	0.66	1.29	2.5
In alloy casting	5.9	3.4	9.6	6.4	36.3
Total	9.5	7.7	10.3	7.7	38.8
Amount of element added	10.06	8.56	12.02	9.13	38.8
Percentage loss	5	10	14	15	0

The loss of from 5 to 15 per cent of each fission product element may be attributed to crucible losses or to sampling and analytical error.

Preparation of Plutonium - 9.5 Atomic Per Cent Iron Fissium Alloy

Plutonium-iron alloy was prepared by heating 26.01 g. of iron and 1061 g. of plutonium in a tantalum crucible in the vacuum induction furnace. This mixture was held at 960°C. for 1 hr. During cooling a sharp thermal arrest was observed at the peritectic temperature of 410°C. After cooling to room temperature, the crucible was removed and chemical analysis of the ingot indicated that the iron was uniformly distributed.

Fissium alloy was prepared by melting the 9.5 atomic per cent iron alloy with typical fission product elements in a tantalum crucible and holding the melt at 1000°C. for 3 hr. in the vacuum induction furnace. On cooling, a thermal arrest was observed at 390°C. After alloying, the fissium was remelted in a magnesia bottom-pour crucible, heated to 1000°C., and chill-cast into a copper mold to form two 5/8 in. diameter cylindrical rods. The rods were then cut into 1 in.-lengths weighing approximately 85 g. each, and samples from each rod were analyzed chemically. A metallographic sample was also taken from the center of Rod No. 2. In Table 3 the chemical compositions of the samples are compared with theoretical and added amounts of each element. The excess of each element

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

added was estimated from previous experience with plutonium-cobalt fissium preparation.

Table 3

COMPOSITION OF IRON-FISSIUM ALLOY

Sample	Concentration of Element, w/o					
	Zr	Mo	Ru	La	Ce	Fe
Rod No. 1 - Top	0.94	0.77	1.34	1.36	0.95	2.72
Center	1.06	0.88	1.32	2.40	0.94	2.90
Bottom	0.82	0.73	1.32	1.27	0.91	2.63
Average	0.94	0.79	1.33	1.68	0.93	2.75
Rod No. 2 - Top	0.85	0.77	1.35	1.27	0.90	2.87
Upper Center	0.82	0.73	1.26	1.46	0.81	2.69
Lower Center	0.82	0.74	1.27	1.28	0.67	2.71
Bottom	0.80	0.71	1.25	1.22	0.56	2.75
Average	0.82	0.74	1.28	1.31	0.74	2.76
"As-added"	0.94	0.93	1.35	2.46	1.06	2.50
Theoretical for 10% burnup	0.79	0.77	1.13	1.90	0.78	2.50

NOTES: 1. Lanthanum was used as a stand-in for all rare-earth fission products except cerium.

2. The "theoretical for 10% burnup" fission product percentage concentrations are slightly high because all of the fission products have not been added. However, these concentrations correspond to the correct amount of element per unit weight of plutonium.

Although the distribution of fission product elements shown in Table 3 was not uniform, the metallographic specimen indicated that the added elements had all been in solution at 1000°C. Therefore, the alloy was used for pyrometallurgy experiments.

The composition of each 85-g. ingot was based on samples taken from the same region of the chill-cast rods, rather than on average rod composition.

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

4. LIQUATION EXPERIMENTS

If a fission product element is present in an amount that exceeds the equilibrium solubility, it should be possible to effect a separation simply by holding the fissium in the molten state and allowing insoluble constituents to float to the top of the melt. Moreover, there will result some self-slagging because of small amounts of oxide, carbide, and nitride contaminants normally present in the plutonium used to make the alloy.

Cobalt-Fissium Alloy

Three liquation experiments in which cobalt alloy was used are summarized in Table 4. In the first two experiments (L-1 and L-2), approximately 85 g. of alloy was held in the molten state at 480°C. for 2 hr. in a magnesia crucible (Fig. 3) under a purified helium atmosphere. In the third experiment (L-3) the same amount of alloy was held at 650°C. for 78 hr. in a 1 in. diameter tantalum crucible under vacuum. All three experiments were conducted in a resistance furnace to minimize stirring. During experiment L-3, a small leak developed overnight and 9 g. of oxide was formed on the surface of the melt.

After each liquation, the melt was cooled to room temperature and the crucible was removed. The ingot was then sampled in an inert atmosphere by mounting in a lathe chuck and machining approximately 2 g. of chips for each sample. Core samples were taken by drilling. The small amount of oxide discoloration was removed from the ingot surface before each sample was taken.

From the results shown in Table 4 it appears that zirconium and molybdenum are in excess of equilibrium amounts at 480°C. Cerium, cobalt and, perhaps, ruthenium are relatively unaffected by liquation. The high cerium loss in experiment L-3 was undoubtedly due to oxide formation. A sample of the oxide crust indicated that there was a 5-fold enrichment of cerium in this phase.

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

Table 4

EFFECT OF LIQUATION ON THE COMPOSITION OF COBALT FISSIUM

Experiment No.	Ingot Region Sampled	C/C_o (1) Zr	Mo	Ru	Ce	Co
L-1 (2 hr. at 480°C.)	Top	1.22	1.07	1.06	....	0.94
	Core	0.75	0.68	0.90	0.98	1.00
	Bottom	0.25	0.28	0.77	0.98	0.96
L-2 (2 hr. at 480°C.)	Top	1.08	1.05	1.14	1.07	0.92
	Core	0.98	1.00	0.95	1.03	0.98
	Bottom	0.15	0.36	0.83	1.03	1.00
	Skin	1.11	1.06	1.07	1.22	1.01
L-3 (18 hr. at 650°C.)	Top	0.88	0.82	1.38	0.01	1.27
	Core	0.76	0.64	1.04	0.07	1.01
	Bottom	0.69	0.67	1.13	0.01	1.08

(1) C = Concentration of element in sample after processing.

C_o = Concentration of element in sample before processing.

Iron-Fissium Alloy

One liquation experiment (L-4) was conducted with iron-fissium alloy wherein the melt was held in the vacuum resistance furnace for 18 hr. at 445°C. in a magnesia crucible. After cooling, the ingot was sampled for chemical composition and a piece of the top was metallographed.

Relative changes in composition are shown in Table 5. A comparison of these results with those reported in Table 4 indicates that lanthanum affected the distribution of both cerium and iron. In the absence of lanthanum (cobalt fissium), cerium and cobalt concentrations were unaffected by liquation. It appears that lanthanum partially extracts cerium and iron from iron-fissium alloy.

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

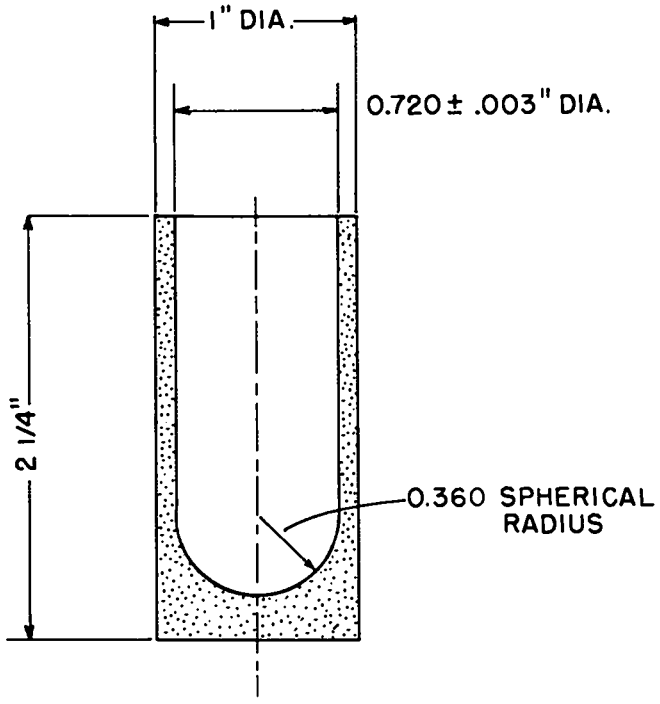


Fig. 3. MAGNESIA CRUCIBLE, TYPE A-392
Dry Pressed, Fired Density Range: 2.8 to 3.0 g./cc.
Maximum Impurity: 1 to 2 Per Cent Silica

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

Table 5

EFFECT OF LIQUATION ON THE COMPOSITION OF IRON FISSIUM
(Expt. L-4, 18 hr. at 445°C.)

Ingot Region Sampled	C/C_o					
	Zr	Mo	Ru	La	Ce	Fe
Top surface	1.68	1.39	1.50	1.93	1.50	1.05
Upper section	1.39	1.19	1.04	1.15	1.18	0.95
Core	1.15	1.07	1.03	1.01	1.25	0.91
Bottom surface	0.01	0.24	1.03	0.15	0.92	0.76

NOTE: Upper-section sample taken just below metallographic specimen.

The metallographic specimen taken from the ingot top indicated that liquation caused a large increase in impurity segregation, as compared to the chill-cast material. Distinct impurity particles varying in size from a few microns to about 1000 μ were distinguishable in the liquated specimen, but not in the original chill-cast alloy.

Apparently, good separation of fission product elements within a reasonable time cannot be obtained by liquation alone. However, there is indication that liquation followed by filtration may be beneficial. Consequently, no additional liquation experiments are planned until a suitable filter for molten plutonium is developed.

5. OXIDATIVE SLAGGING

This method, which has been studied extensively with uranium fuels by Feder and co-workers,[3] consists of holding the molten impure metal in an oxide crucible for a prolonged period to allow oxidation of impurities by reaction with the crucible material. Some fission product removal is affected by formation of an oxide dross at the crucible-melt interface. Equilibrium activities of fission products in the oxide phase will be dependent on the relative free energies of oxide formation,

[redacted]

APPROVED FOR PUBLIC RELEASE

that is, the more negative the free energy, the greater the tendency to concentrate in the slag. The free energy data[7] shown in Fig. 4 indicate that rare earths should be concentrated relative to plutonium in the oxide phase, whereas ruthenium and molybdenum should be concentrated in the melt. There may also be some concentration of zirconium in the oxide phase.

Several oxidative slagging experiments were conducted with both cobalt and iron fissium. The experimental procedure consisted of placing ~85 g. of metal in a type A-392 magnesia crucible (Fig. 3) and heating in the vacuum induction furnace. After the melt was held at temperature for the desired time, the material was allowed to cool to room temperature and the ingot was recovered by breaking the crucible. The ingot was then transferred to the inert atmosphere lathe enclosure for sampling by the procedure described previously.

Cobalt-Fissium Alloy

Results obtained with cobalt alloy (Table 6) indicate that oxidative slagging was ineffective at 1000°C. However, when the temperature was increased to 1380°C., more than 98 per cent of the cerium was removed from the core in 2 hr. This temperature effect is consistent with the free energy data shown in Fig. 4. At 1270°K., magnesia is about as stable as cerium(III) oxide. However, above the normal boiling point of magnesium metal (~1390°K) cerium(III) definitely forms the more stable oxide. This was also indicated experimentally by a heavy magnesium deposit on the inside of the cold Pyrex tube during experiment PCF-7.

The small amounts of zirconium and molybdenum that were removed may be due to self-slagging with carbide, nitride, or oxide impurities in the alloy.

Ruthenium concentration was unaffected by oxidative slagging, except for the metal skin sample in experiment PCF-6. However, because this result on the skin sample is inconsistent with all other data for ruthenium, it is probably in error.

[redacted]

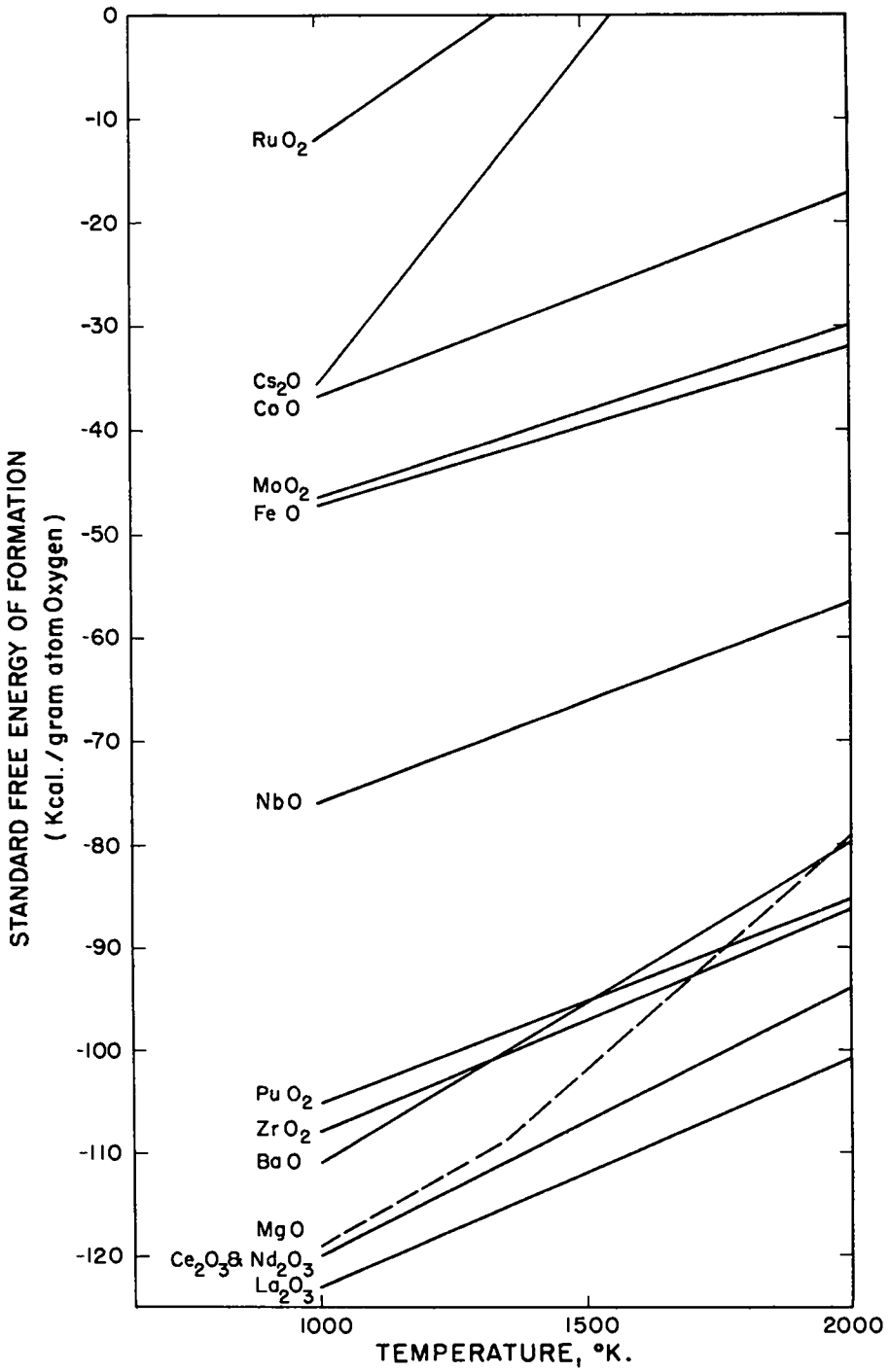


Fig. 4. STANDARD FREE ENERGY OF FORMATION OF THE OXIDES OF SOME TYPICAL FISSION PRODUCT ELEMENTS

[redacted]

[redacted]

Table 6

EFFECT OF OXIDATIVE SLAGGING ON THE COMPOSITION OF COBALT FISSIUM

(Magnesia Crucible, Type A-392)

Experiment No.	Ingot Region Sampled	C/C$_o$				
		Zr	Mo	Ru	Ce	Co
PCF-5	Metal skin	0.88	0.70	0.91	1.00	0.92
(4 hr. at 1000°C.)	Metal core	0.86	0.82	0.96	1.00	0.97
PCF-6	Oxide skin(1)	<0.1	<0.2	<0.06	18.	<0.03
(0.6 hr. at 1300°C.)	Metal skin	0.96	0.76	0.57	0.34	0.90
	Metal core	1.15	0.70	1.00	0.82	0.88
PCF-7	Oxide skin(2)	2.2	<0.2	<0.06	32.	0.03
(2.0 hr. at 1380°C.)	Metal skin	0.84	0.67	1.00	0.09	0.97
	Metal core	0.84	0.73	1.00	<0.02	0.99

(1) Analysis indicated 11 w/o cerium oxide, 88 w/o plutonium oxide.

(2) Analysis indicated 21 w/o cerium oxide, 77 w/o plutonium oxide, and 1.5 w/o zirconium oxide.

Iron-Fissium Alloy

Four oxidative slagging experiments using iron-fissium alloy are summarized in Table 7. The results are similar to those obtained with cobalt fissium (Table 6). Apparently, a temperature greater than 1200°C. is required for good removal of rare-earth elements within a reasonable time. However, the relative rare-earth removals in 2 hr. appear to be less for iron fissium (Expt. PIF-10) than for cobalt fissium (Expt. PCF-7, Table 6). This is because the cobalt alloy originally contained only 0.62 w/o total rare earths. After experiment PIF-10, the total rare-earth concentration was decreased to 0.88 w/o, which represents an absolute decrease of 1.44 w/o. In experiment PCF-7, the absolute decrease was only 0.61 w/o; therefore, the absolute rare-earth removal was greater in experiment PIF-10, perhaps due to the higher rare-earth concentration, and to the slightly higher temperature.

[redacted]

APPROVED FOR PULBIC RELEASE

[redacted]

Lanthanum in the iron-fissium melt also appears to have segregated owing to liquation. In experiments PIF-10 and -11, metal top samples contained considerably more lanthanum than the core samples. During experiment PIF-10, a crust weighing approximately 1 g. was formed above the ingot as a "skull." Zirconium, lanthanum, cerium, and iron were enriched in this "top dross" sample, presumably due to both slagging and liquation processes operating simultaneously. This would indicate that liquation followed by mechanical separation should be done prior to oxidative slagging. Otherwise the rare-earth elements may concentrate in a surface layer having a small crucible area/liquid metal mass ratio, which would decrease the total rate of oxide formation.

As in the cobalt-fissium experiments, zirconium, molybdenum, and ruthenium concentrations were not greatly affected by oxidative slagging. However, the tendency for zirconium to segregate was indicated by the metal top sample of experiment PIF-11.

Table 7

EFFECT OF OXIDATIVE SLAGGING ON THE COMPOSITION OF IRON FISSIUM

(Magnesia Crucible Type A-392)

Experiment No.	Ingot Region Sampled	C/C_o					
		Zr	Mo	Ru	La	Ce	Fe
PIF-9 (2 hr. at 1200°C.)	Metal skin	0.99	0.96	1.00	1.28	1.30	1.06
	Metal core	0.79	0.67	0.99	0.44	0.89	1.10
PIF-10 (2 hr. at 1420°C.)	Top dross	3.00	0.7	0	6.3	1.5	1.9
	Oxide skin	0.57	0.54	<.05	22.	7.7	0.78
	Metal top	1.09	1.22	0.93	2.14	1.34	0.89
	Metal core	0.79	0.73	0.90	0.26	0.62	1.06
	Metal skin	0.93	0.96	0.96	0.55	0.43	0.96
PIF-11 (5 hr. at 1440°C.)	Oxide skin	1.73	0.41	0.11	28.	9.3	0.26
	Metal top	2.80	0.77	0.81	2.03	2.83	0.79
	Metal core (1)	0.74	1.00	1.07	<.05	0.05	....
	Metal skin	0.79	0.86	0.92	0.45	0.74	0.95
PIF-12 (3 hr. at 1470°C.)	Oxide skin (2)	0.09	<.03	0.01	41.	12.7	0.17
	Metal top	1.06	1.33	1.02	<.15	0.32	1.61
	Metal core	1.14	1.37	1.04	<.07	0.27	1.14
	Metal bottom	0.90	1.11	0.94	<.09	0.30	1.11

(1) Concentration of magnesium in processed ingot core sample was <0.1 w/o.

(2) Plutonium concentration in oxide skin was 20 w/o.

[redacted]

APPROVED FOR PUBLIC RELEASE

[redacted]

Effect of Oxidative Slagging on Rare-Earth Elements

The removals of lanthanum and cerium by oxidative slagging are summarized in Table 8. For the concentrations used in these experiments, a slagging time of about 4 hr. at 1450°C. would be required to reduce total rare-earth concentration by a factor of at least 10. Type A-392 magnesia crucibles having a wetted area of 0.17 sq. cm. per gram of liquid fissium were used in all slagging experiments.

Table 8

EFFECT OF TIME AND TEMPERATURE ON RARE-EARTH REMOVAL BY OXIDATIVE SLAGGING

Experiment No.	Time, hr.	Temp., °C.	C/C_o		
			La	Ce	TRE(1)
PIF-9	2	1200	0.44	0.89	0.58
PIF-10	2	1420	0.26	0.62	0.39
PIF-12	3	1470	<0.07	0.27	<0.15
PIF-11	5	1440	<0.1	0.06	<0.07

(1) Total Rare Earths.

Effect of Oxidative Slagging on Radioactive Fission Product Elements

In using fissium alloy as a stand-in for high-burnup fuel, all results are subject to the criticism that elements generated in the fuel by fission may behave differently from added macro amounts of the synthetic fissium alloy constituents. For example, the particle size of added inert elements may be quite different from that of the fission product isotopes of the element.

In order to compare the behavior of fission products with that of added elements, the fissium ingot used in experiment PIF-12 was "tagged" in the following way. A 110 mg. specimen of plutonium was bombarded with thermal neutrons to give approximately 2×10^{13} fissions. This specimen was then alloyed with 110 g. of iron-fissium alloy by holding at 1000°C. for 30 min. in the vacuum induction furnace. (After this operation a

[redacted]

APPROVED FOR PULBIC RELEASE

gamma radiation background was detectable by survey meter on the inside of the furnace cold parts, due to fission product volatilization.) The resulting ingot was sampled at various regions to determine the concentrations of radioactive isotopes of zirconium, ruthenium, and cerium, as well as the concentrations of the macro constituents, zirconium, molybdenum, ruthenium, lanthanum, cerium, and iron. After the slagging experiment, the ingot was sampled and analyzed again for both radioactive and inert constituents. Because the rate of oxide formation is dependent on the concentration of element in the melt, different removals should be obtained by the two analytical procedures if the fission product isotopes of an element are segregated from the inert isotopes in the melt. On the other hand, if the isotopes are not segregated, the same results should be obtained.

Behavior of the radioactive fission product elements is shown in Table 9. The reduction to 29 per cent of the original radioactive cerium concentration in experiment PIF-12 is in close agreement with the reduction of the added nonradioactive cerium indicated in Table 7.

Fission product cerium was enriched in the oxide phase by a factor of 11, which is within analytical error of the 12.7-fold enrichment of inactive cerium shown in Table 7. Fission-product zirconium and ruthenium behaved in the same way as the inactive elements.

Radiochemical results for molybdenum and lanthanum are not available. Because of the short molybdenum-99 half-time (67 hr.), this isotope had decayed to an insignificant activity in the processed ingot samples. Radioactive lanthanum-140 was not determined because the behavior of its longer-lived parent, barium-140, during slagging is unknown. Therefore, results based on radioactive lanthanum would be ambiguous.

A further test of isotopic distribution can be made by computing the specific activity of an element in each sample. If there is no isotopic segregation, processing should not significantly alter the specific activity. As shown in Table 10, the specific activities of most of the samples were unchanged by oxidative slagging.

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

Table 9

EFFECT OF OXIDATIVE SLAGGING ON CONCENTRATIONS OF RADIOACTIVE FISSION PRODUCTS IN FISSIUM ALLOY (EXPERIMENT PIF-12)

Ingot Region Sampled	C/C_o		
	Zr	Ru	Ce
Top	1.08	1.00	0.29
Core	1.08	1.07	0.28
Bottom	0.93	1.04	0.29
Oxide skin	<0.001	<0.001	11.

NOTE: Zirconium-99 was gamma-counted and corrected for decay by using the standard 65-day half-time. A mixture of cerium-141 and -143 was gamma-counted and corrected for decay by using empirical decay data obtained on separate specimens of fissioned plutonium. This method of correction was further checked by counting the core sample from the unprocessed ingot at the same time that the core sample from the processed ingot was counted. The same concentration ratio was obtained. A mixture of ruthenium-103 and -106 was also gamma-counted and corrected for decay by using separate empirical decay data.

Table 10

SPECIFIC ACTIVITIES OF FISSION PRODUCT ELEMENTS BEFORE AND AFTER OXIDATIVE SLAGGING (EXPERIMENT PIF-12)

Ingot Region Sampled	Specific Activity, c./m./μ g. element(1)					
	Zr		Ru		Ce	
	Before	After	Before	After	Before	After
Top	60	60	120	110	260	130
Core	60	50	110	120	170	150
Bottom	245(2)	40	110	120	150	150
Metal skin	50	..	110	...	150	...
Oxide skin	..	..	...	...	...	120

(1) The radioactivity of each element in the "after" samples has been corrected for decay to the time that the "before" samples were counted. See note in Table 9 for method of correction.

(2) The wet chemical analysis on this sample is inconsistent with other results and is probably too low. This would result in a high specific activity.

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

From these results it is apparent that fissium is a satisfactory stand-in for high-burnup fuel. However, it should be noted that the same results would have been obtained if there had been segregation of the radioactive elements, followed by isotopic exchange to the point of equilibrium.

6. CARBIDE SLAGGING

One carbide slagging experiment (PCF-8) was conducted to test the effectiveness of this method for zirconium removal. Approximately 80 g. of cobalt-fissium alloy was held under vacuum in a magnesia crucible for 2 hr. at 1000°C. with a 3/8 in. diameter graphite rod immersed 1/4 in. into the melt. The graphite rod was removed after 2 hr. and the melt was cooled to room temperature. Samples of the carbide skull and of the metal skin (after removing the small amount of oxide) were taken in addition to the usual samples. The results shown in Table 11 indicate that zirconium concentrated in the carbide skull, as well as in the metal skin and bottom. The concentration of zirconium in the core sample was reduced to 60 per cent of the original. Although this represents an improvement over the zirconium removal obtained by oxidative slagging, it is still insufficient. Moreover, a large amount of plutonium carbide was formed in the skull and in the ingot metal skin. Apparently carbide slagging by this procedure is not a promising pyrometallurgical method.

Table 11

EFFECT OF CARBIDE SLAGGING ON THE COMPOSITION OF COBALT FISSIUM
(Experiment PCF-8)

Ingot Region Sampled	C/C_o				
	Zr	Mo	Ru	Ce	Co
Carbide skull	2.29	0.79	0.81	0.71	0.82
Ingot core	0.60	1.00	1.10	0.65	1.09
Ingot bottom	2.00	0.82	0.97	0.94	0.94
Ingot metal skin	1.46	1.12	0.91	0.79	0.91

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

[redacted]

7. FLUORIDE SLAGGING

Two fluoride slagging experiments (PCF-9A and -9B) were conducted with cobalt-fissium alloy. In each experiment, the alloy (~40 g.) was melted in a cobalt(II) difluoride crucible in a helium atmosphere and only the ingot core was sampled after processing. The results shown in Table 12 indicate that good cerium removal was obtained at 900°C. Experiments with iron-fissium alloy also will be conducted.

Table 12

EFFECT OF FLUORIDE SLAGGING ON THE COMPOSITION OF COBALT FISSIUM

Experiment No.	C/C_o				
	Zr	Mo	Ru	Ce	Co
PCF-9A (30 min. at 550°C.)	0.81	0.85	0.91	1.03	0.93
PCF-9B (60 min. at 900°C.)	0.71	0.88	1.13	<0.08	1.65

8. FUTURE EXPERIMENTAL PROGRAM

The following projects are being investigated experimentally to determine suitability for pyroprocessing of iron-fissium alloy. No analytical data are available at this time for any of these experiments.

Liquid Metal Extraction

The removal of fission product elements from uranium by liquid rare-earth metals and by liquid silver has been investigated by Voigt and co-workers.[6]

Several experiments with plutonium-iron fissium have been completed using a lanthanum-iron alloy as the extractant. Other extractants which are being considered are calcium, magnesium, mercury, and thallium.

Slagging Methods

In addition to oxidative slagging, the use of salts (particularly halides) as slagging agents is also being investigated.

[redacted]

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PULBIC RELEASE

UNCLASSIFIED

Methods Involving Complete Oxidation of the Plutonium, Followed by Reduction

Purification of uranium by electrorefining has been discussed by Niedrach and Glamm.(8) Presumably, it should be possible also to purify spent plutonium fuel by a similar method. At the present time, equipment and procedures are being tested with nonradioactive salts.

As distinguished from electrorefining, it may also be possible to effect a purification by completely converting the plutonium to a compound (such as a halide) that can be reduced by electrolysis. The use of selective reductants, such as calcium and magnesium, is also being investigated.

9. REFERENCES

1. LAMPRE - Los Alamos Molten Plutonium Reactor Experiment Proposal, R. M. Kiehn, Los Alamos Scientific Laboratory Report LA-2112, May 1957.

2. High Temperature Fuel Processing Methods, E. E. Motta, Paper P/542 in Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 9, p. 596, United Nations, New York, 1956.

3. Pyrometallurgical Processing of Nuclear Materials, H. M. Feder, Paper P/544 in Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 9, p. 586, United Nations, New York, 1956.

4. The High Temperature Processing of Metallic Fuels, F. S. Martin and G. L. Miles, Great Britain Atomic Energy Research Establishment Report AERE-C/R-1628 (RCTC/P-43).

5. Application of High Temperature Processing to Fast Reactors, J. M. Fletcher and T. M. Fry, Great Britain Atomic Energy Research Establishment Report RCTC/P-60, Jan. 10, 1956.

6. Liquid Metal Extraction for Processing of Spent Fuels, A. F. Voigt et al., A. I. Ch. E. Journal, 2, 169-73 (1956).

7. A Survey of the Free Energies of Formation of the Fluorides, Chlorides, and Oxides of the Elements to 2500°K., Alvin Glassner, Argonne National Laboratory Report ANL-5107, August 1953.

8. Electrorefining as a Method for Removing Fission Products from Uranium Fuels, L. W. Niedrach and A. C. Glamm, Paper 200 in Nuclear Engineering and Science Congress, December 1955.

UNCLASSIFIED

APPROVED FOR PUBLIC RELEASE