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<i>H. F. Canale</i>	
Chief, Declassification Branch	

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EDITED BY:

E. E. Motta
D. W. Bareis
D. D. Cubicciotti

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ABSTRACT

Work has continued on high temperature methods for processing irradiated uranium fuel. Additional results have been obtained with fused halide treatment, solid scavengers and direct Pu distillation. With fused fluorides about 95 per cent of the Pu was removed from a uranium sample, while treatment of uranium with HCl gas removed almost all the Pu and many fission products. Treatment of molten uranium with uranium oxide removed a substantial fraction of the fission products without removing Pu. Uranium carbide treatment results were similar to the oxide but not as effective. A small scale distillation of Pu from uranium showed that Raoult's law is obeyed,

This report is based on studies conducted for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

Previous Quarterly Reports in This Series

- NAA-SR-220 Separations Chemistry Progress Report for Period
October, November, December, 1952
- NAA-SR-245 Separations Chemistry Quarterly Progress Report
January - March, 1953
- NAA-SR-273 Separations Chemistry Progress Report for Period
April, May, June, 1953
- NAA-SR-844 Separations Chemistry Quarterly Progress Report
July - September, 1953

I. INTRODUCTION

The research program under study by the Separations Chemistry Group is chiefly concerned with the development of high temperature processes for extracting fissionable elements such as Pu from fertile reactor fuel sources and for separating fission products from reactor fuels.

This report includes recent work on the direct distillation of Pu from U, the removal of fission products and Pu from U by solid scavengers and fused salts, and studies of the decontamination of U using other metals.

II. HIGH TEMPERATURE COMPACT SEPARATIONS METHODS FOR NUCLEAR FUELS

A. Decontamination of Uranium with Fused Halides

1. Fluorides (A. G. Buyers) - Investigation of tracer plutonium and fission product distribution between equilibrated molten uranium and various fused salts or salt mixtures was continued this quarter. Experiments were carried out with 5 to 15-gram samples of irradiated uranium ($nvt = 10^{16}$) which were contained in graphite crucibles and fused with 3 to 4 grams of salt at 1300°C under 1 atmosphere of helium. The calcium fluoride equilibrations were conducted in a metal vacuum system enclosed within a glove box in preparation for experiments with higher levels of Pu activity. The fusion chamber area is shown in Fig. 1.

Plutonium distribution data obtained are summarized in Table I. The data shown for pure UF_4 were obtained earlier and are included for comparison. Lithium fluoride was added to cerium fluoride and calcium fluoride scrubs to lower their melting points either through double salt or eutectic formation.

Plutonium extraction into the salt phase was good in all cases. Because the free energies of formation per equivalent calculated for CeF_3 , CaF_2 and LiF were more negative than that for PuF_3 , the presence of plutonium in the salt after equilibration was probably due to small concentrations of uranium fluoride formed during equilibration. This opinion was supported by compari-

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Fig. 1. Fusion Chamber Area of Glove Box Vacuum System

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TABLE I
PLUTONIUM DISTRIBUTION OBTAINED BY EQUILIBRATING
MOLTEN URANIUM WITH FUSED FLUORIDES AT 1300° C

Salt Mixture Introduced, Composition, mole %	Per Cent Found			
	Salt after Equilibration	Metal from Equilibration	Removed from Metal	Activity Balance %
CeF ₃ - 10.9 } LiF - 89.1 }	84	11	89	95
CaF ₂ - 26.2 } LiF - 73.8 }	89	11	89	100
CaF ₂ - 24.5 } LiF - 73.3 } UF ₄ - 0.2 }	95	6	94	101
UF ₄ - 100	87	7	93	95

son of the data reported in Table I for treatment of molten uranium with CaF₂-LiF and CaF₂-LiF-UF₄. The latter experiment showed greater plutonium removal from the metal and a larger percentage present in the salt melt after processing.

Fission product distribution percentages are represented in Table II. These data show that cerium and the rare earth elements were appreciably extracted into salt, strontium and barium were only slightly extracted from the metal by equilibration with the cerium-lithium fluoride and in general the uranium fluoride was more effective in removing fission products than the cerium-lithium mixture.

2. Chlorides (W. A. Rosser, Jr.)

a. A second uranium chloride evaporation experiment similar to that described in the previous progress report (NAA-SR-844) resulted in removal of plutonium, the rare earth elements and the alkaline earth elements from irradiated uranium metal. In this experiment the uranium was powdered by a hydride treatment, the powder treated with HCl gas, and the mixture

TABLE II

TRACER FISSION PRODUCT DISTRIBUTION IN FUSED FLUORIDE
EQUILIBRATIONS WITH MOLTEN URANIUM AT 1300° C

Fission Product	% Activity							
	UF ₄				CeF ₃ - 10.9 mole % LiF - 89.1 mole %			
	Salt	Metal	Removed from Metal	Material Balance	Salt	Metal	Removed from Metal	Material Balance
Ce	71	26	74	101	103	20	80	123
R. E.	58	32	68	90	49	53	47	102
Sr	47*	33*	67*	80*	20	82	18	102
Ba	-	32*	68*	-	20	88	12	108

*Extracted from "Separations Chemistry Progress Report for Period April, May, June, 1953," NAA-SR-273, December 1, 1953, page 13 for purposes of comparison.

heated above the melting point of uranium. In both experiments about 6 per cent of the uranium metal was converted to UCl_3 but in the latter experiment the conversion was accomplished in 2 steps. The results are shown in Table III.

TABLE III

DISTRIBUTION OF ACTIVITY IN 2-CYCLE UCl_3 -
EVAPORATION EXPERIMENT

Element	% Activity		
	Metal	Salt	Crucible
Pu	<1	99	1
R. E.	<1	97	1
Ba	2	102	1
Sr	1	99	1
Nb	97	9	2
Zr	98	1	2
Ru	101	0	0

Although 6 per cent of the uranium metal was converted to UCl_3 in the course of the experiment, this figure could be considerably reduced by increasing the number of cycles and decreasing the amount of the salt formed in each cycle.

b. Treatment of liquid uranium metal with liquid calcium chloride removed only a portion of the plutonium. Fifty per cent of the plutonium content of a 7-gram sample of uranium was removed by treatment with 3 grams of calcium chloride. The addition of small to moderate amounts of AgCl to the calcium chloride used as above improved the removal of plutonium from about 50 per cent to 75 to 80 per cent because of the presence of UCl_4 in the salt phase. The small amount of silver which also results from the reaction:

may however, hold back some of the plutonium. In another experiment 100 mg of UCl_3 was made directly from U and HCl . This was added to 1.5 grams of CaCl_2 and the mixture fused with irradiated U at 1225°C under about 75 mm of He. About 65 per cent of the Pu was removed from the uranium.

B. Distillation of Plutonium from Molten Uranium

1. Scale-up Work (J. R. Foltz, W. Gardner, F. Rosen) - This quarter has been spent in procurement, design, and construction of equipment to be used for the distillation of plutonium from approximately one kilogram quantities of uranium fuel. These experiments will be carried out in the NAA hot cells and the equipment should be ready for operation as soon as the hot cells are completed. The furnace will be used for other high temperature separations methods in addition to the plutonium distillation process.

Procurement of materials is complete except for several small items. The design of the apparatus has been completed except for the condenser leaching tank and the liquid sampling system. Construction of components for the vacuum system is complete and the supporting framework is being assembled.

The problems of sampling the crucible and ingot after distillation and cooling have been worked out. The crucible will be sampled with a diamond core drill driven by a 56 rpm Bodine motor. The ingot will be sampled by an electrolytic drilling technique which is similar to electropolishing. In test runs 1/8 inch diameter holes have been drilled in uranium metal at the rate of

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Fig. 2. Operational Flow Sheet for Pu Distillation Scale-up Experiment

Top Surface (90X)

Bottom Surface (50X)

Fig. 3. Photomicrographs of Uranium Melted in UO_2 Crucible

Interior (200X)

Interior (110X)

Fig. 4. Photomicrographs of Uranium Melted in UO_2 Crucible

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Fig. 6. Glove Box for High Pu Level Experiments with Solid Scavengers

approximately 0.002 inch per minute. Both these methods will give fairly representative samples if several cores are used and the total sample can still be confined to about 2 per cent of the ingot or crucible.

Figure 2 shows the operations and processes to be carried out during the experiment. Figures 3 and 4 show photomicrographs of sections of a uranium ingot which was held at 1700° C for 2 hours in a UO₂ crucible. With the exception of the surface, which showed inclusion of precipitated oxide, the metal was very clean.

2. Evaporation from Pieces of X-10 Slugs (D. D. Cubicciotti) - The evaporation of Pu from U is being studied with small pieces of X-10 slugs in order to see if Raoult's Law is obeyed.

The apparatus used is almost identical with that used in the tracer study;* however, the vacuum line is enclosed in a glove box to prevent the spreading of Pu contamination. Figure 5 is a photograph of the system.

To date three experiments at 1680° C have been completed. The results of the first two were low, showing only 90 per cent of the evaporation expected from Raoult's Law. The reason for this was that the bottom of the crucible was too cold because of radiation losses. A bottom radiation shield was included in the third experiment and the fraction evaporated conformed to Raoult's Law quite well. Under conditions in which about 99 per cent of the Pu was expected to evaporate, 98.4 per cent was actually removed.

C. Decontamination of Uranium with Solid Scavengers

1. Uranium Oxide (A. Saul, F. J. Keneshea, Jr.) - Tracer experiments on the extraction of fission product elements from molten uranium by scavenging with solid uranium oxide have been continued. A 3-gram sample of irradiated uranium metal was contacted with three successive portions of uranium oxide. The experimental procedure employed was described in the previous progress report. The results of Pu and fission product analyses of the oxide phases

*Cubicciotti, D. D., "The Volatization of Tracer Plutonium from Molten Uranium Metal," NAA-SR-242, May 22, 1953.

and of the treated metal are reported in Table IV. The percentages reported are based on a control analysis of untreated metal.

TABLE IV
DISTRIBUTION OF ACTIVITY IN 3-CYCLE OXIDE SCAVENGING

Element	Per Cent Activity			
	Treated Metal	1st Oxide	2nd Oxide	3rd Oxide
Ba	0	82	0.5	0.1
Sr	0	86	0.6	0.1
Ce	0	86	4	0.1
R. E.	0	78	1	0.1
Zr	4	65	10	1
Nb	23	83	5	2
Ru	100	0	0	0
Te	0	0.1	0.1	0.1
Cs	2	100	1	1
Pu	87	5 (Total for 3 runs)		

In view of these results on tracer scale, scavenging experiments are being planned on small samples of X-10 slugs. A glove box containing a high vacuum system and provisions for oxidizing and heating uranium fuel samples has been constructed and has been successfully tested. A photograph of this apparatus is shown in Fig. 6.

2. Uranium Carbide (C. T. Young) - Tracer studies of the decontamination of uranium metal at high temperatures by scrubbing with uranium carbide were continued. The description of the procedures and techniques used for the first run is given in the previous progress report (NAA-SR-844). In general, the same techniques were employed for the runs completed during the past quarter.

The uranium carbide used for scavenging was placed on top of the uranium metal in Runs 1 and 2. Since the carbide floated on the metal, the UC_2 came in contact with the portions of the melt which reached the top surface as

Fig. 5. Vacuum Line in Glove Box for High Level Pu Distillations

a result of the stirring action caused by induction heating and convection. Run 3 was made without the addition of uranium carbide to determine the scrub effectiveness of the graphite crucible.

TABLE V
SUMMARY OF CONDITIONS OF UC₂ SCRUB OF MOLTEN U METAL

Run	Crucible Material	Quantity of U Metal g	Quantity of UC ₂ for Scrub g	Placing of UC ₂ for Scrub	Temperature °C	Time of Heating Hour
1	Graphite	3.5	1.4	Above U Metal	1375	1
2	Graphite	21.5	3.2	Above U Metal	1375	1
3	Graphite	13.7	0	None added	1375	1

For radiochemical analysis the uranium carbide scrubs were dissolved by a HNO₃ + HClO₄ solution, the melts by HNO₃ and the crucibles were oxidized by HNO₃ + HClO₄ solution. The averaged results from the runs are summarized in Table VI.

D. Treatment of Uranium with Other Metals for Decontamination

1. Uranium Alloys for Lowering Processing Temperatures

(F. J. Keneshea, S. Yosim)- High temperature processing of metallic uranium fuel by such methods as fused salt scrubbing, solid scavenging and liquid metal extraction requires temperatures above the melting point of uranium (1135° C). At such high temperatures reaction of the container with the molten uranium and/or the processing material can be a problem. The possibility exists that operation at a lower temperature by alloying the uranium with suitable metals might reduce this problem to the point where it does not affect the processing. For example, uranium and nickel form a eutectic at 13 wt per cent Ni which melts 400° lower than pure uranium. With such a system processing can be carried out at 800° C instead of 1200° C. Some other uranium alloys with melting points less than 900° C at a uranium composition greater than 10 wt per cent are: 5 per cent chromium (859° C), 6 per cent manganese (716° C), 12 per cent iron (725° C), 11 per cent cobalt (734° C), and 88 per cent mercury (330° C). The addition of the alloying metal should

TABLE VI
SUMMARY OF THE PERCENTAGES OF ACTIVITIES IN THE
U METAL AFTER A UC₂ SCRUB

Element	Averages of Runs 1* & 2	Run 3†
Mo	100	100
Iodine	6	24
Ru	80	102
Nb	50	93
Zr	35	75
Ce	60	75
R. E.	30	65
Ba	30	83
Sr	30	88
Cs	25	103
Te	15	
Pu	100	

*Extracted from "Separations Chemistry Quarterly Progress Report, July-September, 1953," NAA-SR-844, April, 1, 1954.

†No UC₂ added (control)

not interfere with either the fused salt scrubbing or solid scavenging processes and perhaps will not interfere in liquid metal extraction.

An experimental study of the feasibility of lowering processing temperature via alloying has been initiated. In addition to studying Pu and fission product removal in a lower temperature system, methods for removing the alloying metal from the uranium will also be investigated. Separation of the added metal should be done in such a manner that the uranium remains in, or can be easily converted to the metallic state. Some of the methods by which this might be accomplished are:

1. Volatilization - This should be suitable for mercury and possibly manganese due to their relatively high vapor pressures.

2. Carbonyl Formation - Nickel would be the most favorable with iron and cobalt also possibilities. If the carbonyls can be formed, they can be distilled from the uranium.
3. Hydride Formation - If the uranium of the iron, nickel or cobalt alloys can be hydrided, it is possible that the alloying metal can be removed with a magnet.
4. Separation with Another Metal - It may be possible to add a third metal which is insoluble in the binary system and which would extract the original alloying metal.

During the past quarter, uranium alloys of Ni, Cr, Co, Fe and Mn have been prepared. A vacuum system for experiments involving the hydriding process has been designed and constructed.

2. Immiscible Liquid Metals (L. Doyle, R. A. Barney) - A method of processing molten uranium fuel which appears promising is the extraction with molten immiscible metals. Investigators at the Ames Laboratory and at the Chalk River Laboratory have found that molten silver removes Pu and certain fission products from molten uranium. The Ames investigators have also used molten cerium and lanthanum with similar results.

Two metals which have not been tested experimentally in liquid extraction investigations, but which appear to be well suited for this type of processing, are calcium and magnesium. Their chief advantages are that they are relatively inexpensive metals, have low neutron cross sections, and can be easily distilled away from molten uranium. A study has been started at NAA which will determine the feasibility of using liquid calcium and magnesium. The vapor pressure of these metals at the melting point of uranium will require special precautions to avoid their loss during the extraction.

A resistance furnace employing a spiral graphite heating element will be used because it allows careful temperature control. A sketch of this furnace is shown in Fig. 7. Either a vacuum or inert atmosphere can be used in the furnace chamber.

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Fig. 7. Furnace Assembly for Liquid Metal Work

III. SUMMARY

1. Treatment of molten uranium with various fused fluorides having no added UF_4 removed 85 to 90 per cent of the Pu. The addition of 0.2 per cent UF_4 increased that figure to 95 per cent.

2. A 2-cycle treatment of uranium with HCl removed essentially all the Pu, rare earth elements, Ba, and Sr and left Zr, Nb and Ru. Treatment by fused CaCl_2 mixtures with and without added UCl_3 removed at best about 75 per cent of the Pu.

3. Construction of equipment for a scaled-up distillation of Pu from molten uranium has been started.

4. A small scale distillation of Pu from a piece of X-10 slug at 1680°C showed that Raoult's Law was obeyed approximately.

5. A 3-cycle treatment of irradiated uranium with UO_2 removed the Ba, Sr, Ce, rare earth elements, Te and Cs, and most of the Zr and Nb. Most of the Pu and Ru were left behind.

6. Treatment of uranium with uranium carbide removed essentially the same fission products as the UO_2 treatment but not to as great a degree.

7. A study was made of the feasibility of lowering process temperatures by alloying the uranium fuel.

8. Equipment has been assembled to study the extraction of Pu and fission products from molten uranium using molten calcium or magnesium.