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PRODUCTION OF THE TRANSPLUTONIUM ELEMENTS AT SAVANNAH RIVER

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by

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PRODUCTION OF THE TRANSPLUTONIUM
ELEMENTS AT SAVANNAH RIVER*

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Research on the transplutonium elements at Savannah River is aimed primarily at large-scale production programs. In recent years, we have demonstrated the capability of operating our reactors at thermal flux levels approaching 10^{16} neutrons/(cm^2)(sec) and with a wide variety of useful production loadings. This capability is currently being exploited to produce 4.5 kg of ^{244}Cm , and might also be used for special production programs involving other transplutonium isotopes. Intensive development of technology is necessary to place these programs on a sound basis so that we know, for example, exactly how much material we will produce at a given cost, and the characteristics of the products that will be obtained. We must also be alert to the possibilities of extracting byproducts that may be of value for research or for special applications. In this talk, I would like to review our progress in the production of ^{244}Cm , and also discuss some of the work that we are doing that should lead to more effective recovery of heavier isotopes either as special products or as byproducts.

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Savannah River became involved in the production of the transplutonium elements in 1959 when a decision was made to irradiate ^{239}Pu in a Savannah River reactor to produce ^{242}Pu , ^{243}Am , and ^{244}Cm that would serve as target materials for subsequent irradiation in the HFIR at Oak Ridge. This program, which was divided into two separate campaigns at Savannah River, extended over a period of about five years. The final shipment of the products to Oak Ridge was made in December 1964. The total quantities of products and the isotopic composition of each are shown on Slide 1. Only the ^{242}Pu was purified; the ^{243}Am and ^{244}Cm were shipped as a crude mixture with the rare earth fission products.

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YIELDS FROM SAVANNAH RIVER TRANSPLUTONIUM CAMPAIGNS

151.2.1.6.

245cm 1.47

not prepared for further
work. reg. 1.47 isotope

300
330
344

When the production of a larger quantity of ^{244}Cm was undertaken in 1963, it was evident that the basic technology developed in the course of the Transplutonium Program would be applicable. At the same time, potential improvements in the irradiation were indicated, and new chemical processes were required to separate americium and curium, both from the rare earth fission products and from each other.

The improved irradiation involves two steps. In the first, ^{239}Pu is irradiated until the content of fissionable isotopes is reduced by about 60%; the plutonium is then separated by chemical processing and refabricated into targets for the second irradiation step at a flux which is increased (as fissionable isotopes are depleted) to about $10^{15} \text{ n}/(\text{cm}^2)(\text{sec})$. This method of irradiation reduces the total reactor time and results in considerably lower production costs.

In preparation for the second step of irradiation, a test of the high-flux operation at Savannah River was made to determine if any difficulties might occur. During this test, ^{242}Pu was irradiated to provide higher isotopes as feed material for the HFIR. Also, special targets were irradiated, including some to produce ^{252}Cf .

The yields of the main products of the Curium Program together with the expected delivery dates are shown on the slide (Slide 2). You will note that additional ^{244}Cm could be produced by irradiating the ^{242}Pu and ^{243}Am intermediates, and indeed this would be done for a continuing curium production program. As a matter of interest, such a continuing program would produce, as a byproduct, about 5 to 10 mg of ^{252}Cf per kg of ^{244}Cm .

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SLIDE 2

MAIN PRODUCTS OF THE CURIUM PROGRAM

Starting Material: Pu (8% ^{240}Pu)

<u>Product</u>	<u>Amount, kg</u>	<u>Date Available</u>
^{242}Pu	9.2	July 1967
^{243}Am	3.0	October 1967 - March 1968
^{244}Cm	4.5	October 1967 - March 1968

Handwritten: 11/3/67

Handwritten notes:
 11/3/67
 3 kg and 1.5 kg Cm²⁴⁴
 and T₁ II
 + M₁
 and T₁ II
 D.P. 1000

For the purification of americium and curium we have adopted the tertiary amine solvent extraction (Tramex process) system originally developed here at ORNL. Americium will be separated from curium by precipitation of the double salt of Am(V) from a potassium carbonate solution.

Our current version of the chemical process that will be used in the separation and purification of the curium is outlined in the following slides. First, (Slide 3) the plutonium is separated from the americium and curium by countercurrent solvent extraction with tributyl phosphate (TBP) as the extractant. Am-Cm and the rare earth fission products in the raffinate are then separated from the large quantity of aluminum by batch extraction with 50% (TBP). The nitric acid solution from this step is then concentrated by evaporation and serves as the feed solution for the first of three cycles of tertiary amine extraction.

The first amine extraction converts the nitrate solution to a chloride system suitable for rejection of the rare earths in the two following Tramex cycles. The second Tramex cycle is included to ensure that no more than 10% of the gamma radiation from the final curium product is due to fission products. This slide also indicates the route of californium through the process—special steps are taken to reject californium, which would otherwise contribute an undesirable neutron emission to the curium product. Practically all of the californium is collected in the slightly acid solvent wash solution from which it may be recovered.

In the early tests and demonstrations at both ORNL and Savannah River, special attention has been given to problems arising from

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SLIDE 3

CURIUM SEPARATIONS

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the high levels of radiation in the process solution. Oxidation of cerium to Ce(IV), which is not separated from Am-Cm by the process, by radiolytically generated hypochlorous acid has been a particularly difficult problem to solve. Process tests show that the addition of Sn(II) to the feed solution reduces the cerium without adversely effecting the overall process. Also, we have studied in some detail the degradation of the tertiary amine-diethylbenzene solvent because we need to recycle the solvent through the process to the maximum practical extent. The results of extended tests indicate that the solvent may be recycled many times without serious damage.

The overall performance of the solvent extraction steps, as measured in small-scale laboratory tests, is summarized here (Slide 4).

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SLIDE 4

PERFORMANCE OF SOLVENT EXTRACTION PROCESSES

	<u>Curium Loss %</u>	<u>Decontamination Factors</u>				
		<u>^{144}Ce</u>	<u>^{154}Eu</u>	<u>^{95}Zr</u>	<u>^{106}Ru</u>	<u>^{252}Cf</u>
Batch Extraction	<2.5	-	-	20	3	-
Conversion Cycle	0.2	-	-	1.5×10^3	490	-
First Tramex Cycle	0.2	2.6×10^3	1.6×10^3	40	73	(10)
Second Tramex Cycle	0.1	5.9×10^4	>500	-	>40	-
Cumulative	<3.0	1.5×10^6	> 8×10^5	> 1×10^6	> 4×10^6	-
Total Required	-	1×10^6	100	2.4×10^4	7×10^5	(10)

In the final steps of the process, americium and curium are separated and converted to the oxides. Ozone has proven to be a useful oxidant for americium in the precipitation step and has been chosen in preference to hypochlorite or persulfate. By the sequence of steps as shown and for a feed solution containing about equal concentrations of curium and americium, the curium product contains less than 0.2 wt % of americium, while the americium fraction contains less than 0.5 wt % of curium.

We are confident that the process will perform well in the processing of the 4.5 kg of curium. At the end of that campaign, we will have a clear demonstration of a process suitable for a very large-scale production program.

I would like to discuss now some cross section studies related to production of the heavier elements. The cross sections of the nuclear reactions of the nuclides beyond ^{244}Cm are dependent upon the neutron spectrum in the reactor. Our experiments are designed to measure cross sections in the highly thermal spectrum of the Savannah River high-flux charges as well as episcadmium cross sections of ^{252}Cf precursors.

Our experimental data are being developed from analysis of (1) target elements of $^{242}\text{PuO}_2$ that were removed from our high-flux charges at exposures of 3.7, 5.3, and 7.0×10^{22} n/cm²; (2) thin targets of selected nuclides or mixtures of nuclides in the ^{242}Pu - ^{252}Cf chain irradiated both with and without cadmium shielding for extended periods at high flux; and (3) thin targets of selected mixtures of nuclides irradiated for very short periods.

The next two slides (Slides 5 and 6) summarize the results of the measurements.

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SLIDE 5

CROSS SECTION DATA FROM SHORT-TERM IRRADIATIONS

<u>Target Foil</u>	<u>Exposure, min</u>	<u>Nuclear Reaction</u>	<u>σ</u>	
			<u>Measured</u>	<u>Published*</u>
^{242}Pu (2 mg)	60	$^{242}\text{Pu} \rightarrow ^{243}\text{Pu}$	23	19
^{243}Am (0.4 mg)	60	$^{243}\text{Am} \rightarrow ^{244\text{m}}\text{Am}$	80	-
		$^{243}\text{Am} \rightarrow ^{244}\text{Am}$	4.3	-
		$^{243}\text{Am} \rightarrow ^{244}\text{Am}$ (total)	84	134
^{249}Bk (0.5 μg)	340	$^{249}\text{Bk} \rightarrow ^{250}\text{Bk}$	660	800 $\pm$ 200
				1100 $\pm$ 300

* Hyde, Perlman, and Seaborg, The Nuclear Properties of the Heavy Elements, Prentice-Hall, 1964.

SLIDE 6

CROSS SECTION DATA FROM SHORT-TERM IRRADIATIONS

<u>Target</u>	<u>Exposure, n/cm²</u>	<u>Nuclear Reaction</u>	<u>σ</u>	
			<u>Measured</u>	<u>Published*</u>
$^{242}\text{PuO}_2$	3.7 and 5.3 x 10 ²²	$^{242}\text{Pu} \rightarrow ^{243}\text{Pu}$	18	19
		$^{243}\text{Pu} \rightarrow ^{244}\text{Pu}$	35	170 ±90
		$^{247}\text{Cm} \rightarrow ^{248}\text{Cm}$	~600	35
		$^{247}\text{Cm} \rightarrow \text{FP}$	~1400	35
		$^{250}\text{Cf} \rightarrow ^{251}\text{Cf}$	~1200	1500
		$^{251}\text{Cf} \rightarrow ^{252}\text{Cf}$	~1600	3000
		$^{251}\text{Cf} \rightarrow \text{FP}$	~3000	3000
^{243}Am (2 mg)	5 x 10 ²¹	$^{243}\text{Am} \rightarrow ^{244}\text{Am}$	66	134
		$^{244}\text{Cm} \rightarrow ^{245}\text{Cm}$	20	25
		$^{245}\text{Cm} \rightarrow ^{246}\text{Cm}$	260	135
		$^{245}\text{Cm} \rightarrow \text{FP}$	~2000	1900

* Hyde, Perlman, and Seaborg, The Nuclear Properties of the Heavy Elements, Prentice-Hall, 1964.

These data not only confirm the importance of the fission losses of ^{245}Cm and ^{251}Cf as limitations on the ultimate capability of irradiations to produce ^{252}Cf , but also show a major fission loss at ^{247}Cm , as well as significant variations from the published capture cross sections for these nuclides. These data emphasize the importance of the neutron spectrum in determining the most effective means of producing the heavier actinides.

Further work that is planned includes irradiation with and without cadmium shielding of ^{246}Cm , ^{248}Cm , and the californium isotopes. Foils of ^{242}Pu , ^{244}Cm , and ^{243}Am are now being analyzed to give data on cross sections in the epithermal region. Finally, the extensive data on yields of the actinides from ^{242}Pu through ^{254}Es that we are measuring in the three high-flux target elements are being fitted in a computer program to yield accurate thermal cross sections for the entire sequence of nuclear reactions.

The production of ^{252}Cf in the resonance region is markedly greater than that in a thermal spectrum. This increased production is illustrated on this slide (Slide 7) which shows the calculated production of ^{252}Cf in a resonance reactor and that in a high thermal flux. You will note that resonance operation shows potential for a 100-fold increase in ^{252}Cf production. In the calculations, experimental resonance integral data were used when available; in the absence of such data, synthetic values were estimated from the formula shown on the slide.

From this type of estimate, one could project production of ^{252}Cf at rates of hundreds of grams per year, and at such rates, one can visualize costs per gram that are nearly as low as those for radium some 25 years ago. Obviously, such a production program

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is not currently possible and would take many years to prepare and execute. However, the existence of this possibility helps one to recognize that continued research on the transplutonium elements is not without practical value.

Finally, I would like to mention Mössbauer spectroscopy, as one of the more unusual tools being exploited to determine nuclear and solid-state properties of the actinides. In 1964, we discovered the Mössbauer effect with the 59.6-keV gamma ray in ^{237}Np , emitted following either the alpha decay of ^{241}Am or the beta decay of ^{237}U . Under suitable conditions, this gamma ray has a high probability of being emitted without recoil, and thus may be resonantly absorbed by ground-state ^{237}Np nuclei, raising the nuclei to the excited state. More recently, we have demonstrated the Mössbauer effect with the 84.2-keV gamma ray in ^{231}Pa , produced in the beta decay of ^{231}Th . We are currently planning experiments with the 83.9-keV gamma ray in ^{243}Am , using ^{243}Pu sources. Future possible Mössbauer studies include ^{242}Cm , ^{244}Cm , ^{246}Cm , ^{248}Cm , ^{249}Bk , and ^{250}Cf , although some of these isotopes offer sizeable experimental difficulties.

The Savannah River Laboratory work has provided the first demonstration of the Mössbauer effect in the actinide elements and following alpha decay. We expect the longrange usefulness to lie primarily in hyperfine spectroscopy, which will permit the study of crystal fields, electronic valence configurations, and magnetic properties of solid actinide compounds. For example, the simple, single-line transition of ^{237}Np can be split by electric quadrupole or magnetic interactions into different neptunium compounds (Slide 8), to give the typical Mössbauer spectra shown. The

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magnitude of the magnetic fields measured is especially notable, as large as $3-5 \times 10^6$ gauss in some compounds. Recent studies have indicated that the different valence states of neptunium have distinctly different chemical shifts in their Mössbauer spectra, and thus may be identified unambiguously. We hope to extend hyperfine spectroscopy studies of this type throughout the rest of the actinides.

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SLIDE 7. PRODUCTION OF CALIFORNIUM

SLIDE 8

HYPERFINE MÖSSBAUER SPECTRA OF ^{237}Np

Excited State
Energy Levels

Ground State
Energy Levels