325
1/20/65

IDO-14649
November 1964

BURNUP DETERMINATION OF NUCLEAR FUELS: 1963 ANNUAL PROGRESS REPORT

MASTER

Edited by
J. E. Rein and W. J. Maeck

PHILLIPS
PETROLEUM
COMPANY

ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PRINTED IN USA. PRICE \$2.00. AVAILABLE FROM THE CLEARINGHOUSE FOR FEDERAL
SCIENTIFIC AND TECHNICAL INFORMATION, NATIONAL BUREAU OF STANDARDS,
U. S. DEPARTMENT OF COMMERCE, SPRINGFIELD, VIRGINIA

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, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

IDO-14649
AEC Research and Development Report
Chemistry
TID-4500 (34th Ed.)
Issued: November 1964

BURNUP DETERMINATION OF NUCLEAR FUELS:
1963 ANNUAL PROGRESS REPORT

Edited By

J. E. Rein and W. J. Maeck

Contributing Personnel

R. M. Abernathey	M. E. Kussy
W. H. Burgus	S. F. Marsh
R. N. Chanda	J. A. Merrill
F. W. Dykes	L. G. Miller
K. T. Faler	T. D. Morgan
R. E. Foster	R. C. Shank
P. Goris	R. R. Spencer
	G. V. Wheeler

PHILLIPS
PETROLEUM
COMPANY

Atomic Energy Division

Contract AT(10-1)-205

Idaho Operations Office

U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

This annual progress report for 1963 describes the status of the project to develop methods for the determination of burnup of nuclear fuels. The emphasis is on high burnup fuels. The major analytical technique being investigated is stable fission product analysis.

SUMMARY

The objective of this project is the development of reliable methods for the determination of burnup of nuclear fuels. Fuels of high burnup, mainly power reactor types, are of primary interest. The major analytical technique that is being investigated is stable fission product analysis.

The reliability of a burnup determination based on the determined abundance of a stable fission product depends on three main factors, on the accuracy of the fission yield value, the amount of the fission product lost by parasitic neutron capture or produced by neutron capture on the A-1 nuclide, and the reliability of the analysis procedure.

Because literature data for the cross sections and the fission yields of stable fission products are either scarce or are in poor agreement, an extensive effort is underway to determine these values.

Capsules have been fabricated for use in the irradiation of stable, enriched, fission product isotopes to obtain cross section values. Bare and cadmium-covered irradiations will be made. Preliminary cross section values were obtained for Pd^{106} .

Fission yields are being measured for U^{233} , U^{235} , Pu^{239} , and Pu^{241} in the thermal neutron energy region. Both in-pile fission counters and capsule irradiations are being used. The latter has greater promise because fission fragment damage to the silicon detector in the in-pile fission counter severely limits the exposure time and hence the production of fission products. A series of capsules, containing known amounts of the four fissionable isotopes, is being prepared. Irradiations with varying levels of burnup are planned which will generate milligram levels of stable fission products.

For fission yield measurements in the fast neutron energy region, a series of capsules containing fissionable isotopes Th^{232} through Pu^{241} had been irradiated in EBR I. Unfortunately, the reactor was shutdown, apparently permanently, before sufficient amounts of the stable fission products had been generated to permit their determination by isotope dilution mass spectrometry.

The fission yield measurement experiments require separation procedures and mass analysis techniques for the stable fission products. A two-stage, triple-filament mass spectrometer was received at midyear. Due to various operational deficiencies, satisfactory operation has not been attained. Chemical separation procedures have been developed for lanthanide elements, palladium, and the inert gases krypton and xenon. Development of a method for long-lived Sr^{90} also is reported.

Compilations of fission yields are presented as a function of neutron energy which indicate the usefulness of various fission products for burnup measurement purposes.

In the conventional method of burnup analysis based on measuring the abundance of a stable fission product, complete recovery from the fuel sample and a quantitative analysis is necessary. Methods of dissolving various fuel types, uranium metal, uranium-aluminum alloy, uranium-zirconium alloy, and UO_2 -stainless steel, were investigated for fission product recovery. Satisfactory acid systems were obtained for these types except the UO_2 -stainless steel. The stability of fission products in acid media was studied for Teflon containers. A tendency was observed for the lanthanides to preferentially adsorb.

The use of ratios of stable fission product nuclides as monitors for burnup is being investigated. With such a technique, quantitative recovery and analysis is not required.

The depletion (loss of fissionable atoms by fission plus capture) of a fuel can be calculated by computational relationships of heavy element isotopes. Usually matched pre- and post-irradiated samples are analyzed by mass spectrometry. To gain a feeling of the magnitude of the error that would be caused by using preirradiation values with large uncertainties, the error in these relationships was propagated. For high enrichment U^{235} fuel, the calculation was found to be tolerant to large uncertainties in the pre U^{236} content and the error depended mainly on the analysis for fissions.

BURNUP DETERMINATION OF NUCLEAR FUELS:
1963 ANNUAL PROGRESS REPORT

CONTENTS

<u>ABSTRACT</u>	ii
<u>SUMMARY</u>	iii
<u>INTRODUCTION</u>	1
<u>MEASUREMENT OF FISSION YIELDS</u>	3
THERMAL ENERGY REGION	3
<u>In-Pile Fission Counter</u>	3
<u>Capsule Irradiations</u>	3
FAST ENERGY REGION	4
<u>MEASUREMENT OF CROSS SECTIONS</u>	5
<u>ANALYTICAL METHODS FOR FISSION PRODUCTS</u>	5
MASS SPECTROMETRY	5
SEPARATION METHODS FOR STABLE FISSION PRODUCTS	6
<u>Lanthanides</u>	6
<u>Palladium</u>	7
<u>Inert Gases</u>	7
SEPARATION METHODS FOR RADIOACTIVE FISSION PRODUCTS	7
<u>Strontium-90</u>	7
<u>Cesium-137</u>	8
<u>FISSION YIELD COMPILATIONS OF VARIOUS FISSION PRODUCTS FOR BURNUP MONITORS</u>	8
<u>USEFULNESS OF RATIOS OF FISSION PRODUCT NUCLIDES OF THE SAME ELEMENT FOR BURNUP DETERMINATION</u>	15
<u>UNCERTAINTIES IN DEPLETION ESTIMATES</u>	15

<u>DISSOLUTION STUDIES OF IRRADIATED FUELS</u>	16
URANIUM METAL AND URANIUM-ALUMINUM ALLOYS	18
URANIUM-ZIRCALOY ALLOYS	19
URANIUM DIOXIDE-STAINLESS STEEL ALLOYS.	19
<u>STORAGE STABILITY OF DISSOLVED FUEL SAMPLES</u>	20
<u>REFERENCES</u>	21

LIST OF TABLES

Table

1	FISSIONABLE NUCLIDES IRRADIATED IN EBR I.	4
2	UNCERTAINTIES IN DEPLETION ESTIMATES.	17
3	RATIOS OF Zr^{97} , Mo^{99} , and Ce^{143} in AQUA REGIA DISSOLVED URANIUM AND URANIUM-ALUMINUM FUEL SPECIMENS	18

LIST OF FIGURES

Figure

1	Fission Yield Ratio $\frac{U^{235} \text{ Fission Neutrons}}{U^{235} \text{ Thermal Neutrons}}$	9
2	Fission Yield Ratio $\frac{U^{233} \text{ Fission Neutrons}}{U^{233} \text{ Thermal Neutrons}}$	10
3	Fission Yield Ratio $\frac{Pu^{239} \text{ Fission Neutrons}}{Pu^{239} \text{ Thermal Neutrons}}$	11
4	Fission Yield Ratio $\frac{Pu^{239} \text{ Thermal Neutrons}}{U^{235} \text{ Thermal Neutrons}}$	12
5	Fission Yield Ratio $\frac{Pu^{239} \text{ Fission Neutrons}}{U^{235} \text{ Fission Neutrons}}$	13
6	Fission Yield Ratio $\frac{Pu^{239} \text{ Fission Neutrons}}{U^{238} \text{ Fission Neutrons}}$	14

INTRODUCTION

In December, 1961, the Division of Reactor Development, USAEC, awarded contracts to the Atomic Energy Division of Phillips Petroleum Company and the Vallecitos Atomic Laboratory of General Electric for a joint project with the objective to develop accurate methods for the determination of burnup of nuclear fuels(a). The emphasis of this project was to be on power reactor fuels rather than on short term, experimental irradiations. At the outset, then, the approach that was selected as the most promising for burnup determination was stable fission product nuclide analysis.

Since the start of the project, the general trend in power reactor fuel technology has been to higher burnup with levels of 10^5 MWD/T now envisioned. As burnup levels increase, the stable fission product approach for burnup analysis increases in applicability. The approach based on radiochemical analysis for such long lived radioactive fission products as Cs^{137} and Sr^{90} loses attractiveness for two reasons. First, the error in the computation of the in-pile decay correction increases. Second, both these nuclides are volatile at temperatures much lower than the fuel operating temperatures so that migration takes place. The approach of computational relationships, which uses ratios of heavy element isotopes determined by mass spectrometer analysis of pre- and post-irradiated samples, loses effectiveness at very high burnups. Of greater significance, though, is that seldom can matched pre- and post-irradiation samples be obtained, especially for a power reactor core in which there are tons of uranium from different batches of isotopic enrichment material.

The degree of reliability obtainable in a burnup determination based on stable fission product analyses depends on the accuracy of the values used for the fission yields for these fission products. The literature values for the chain yields of the fission products from fissionable isotopes Th^{232} through Pu^{241} , at thermal and fast reactor neutron spectra, are spotty and in poor agreement, even for U^{235} and Pu^{239} . Added to this uncertainty in a highly burned-up sample is the nonlinear relationship between the number of fissions and the number of atoms of a fission product nuclide caused by parasitic neutron captures. The captures cause loss if on the nuclide or on any chain precursors and cause gain if on the A-1 chain. Accurate cross section values would aid the calculation of these nonlinear effects. A major effort, then, of the project, is to accurately determine both the fission yields and the cross sections of the stable fission products in the mass regions of promise for burnup analysis.

(a) The progress report for 1962¹ presents a discussion of the burnup analysis problem, a discussion of the planned experimental program, and a summary of experimental work accomplished during that first year. Progress by General Electric has been reported on a quarterly basis.² Progress by Phillips for 1963, reported originally as part of a larger report³, is the subject matter of the present report.

The development of separation and mass spectrometric methods for the determination of stable fission products is necessary for the stable nuclide fission yield experiments. In the development of these methods, applicability to a wide variety of reactor fuels is being considered.

A new approach for burnup analysis, based on the ratio of the number of atoms of two stable fission product nuclides, is being investigated.

The last major areas of investigation are studies of dissolution methods and storage stability of dissolved samples for various types of reactor fuels. A burnup determination, based on chemical analyses for fission products, requires complete dissolution and solution stability of the analyzed-for fission products.

MEASUREMENT OF FISSION YIELDS

As stated in the Introduction, the degree of reliability obtainable in a burnup determination based on stable fission product analyses depends on the accuracy of the values used for the fission yields. Because of conflicting literature data, a major effort is the measurement of fission yields. For the thermal energy region, both in-pile fission counter and capsule irradiations are in progress. For the fast energy region, only capsule irradiations are being undertaken.

THERMAL ENERGY REGION

In-Pile Fission Counter. This phase of the program is being conducted by the Nuclear Technology Chemistry Section. In the contemplated design, the fission detector is a solid state silicon diode and the two foils are 5 μ g and 50 mg of fissionable isotope. The major effort has been the fabrication and testing of detectors to increase their resistance to fission fragment damage in order to generate larger quantities of fission products. In general, the maximum exposure level is about 10^8 fission events. Above this resolution is impaired which results in counting losses. The use of correction factors for higher level exposures is not feasible as each detector reacts differently.

The decision has been made to operate to a level of 10^7 fissions in the thin 5- μ g foil which will result in 10^{11} fissions in the 50-mg foil. This is not sufficient to produce mass spectrometer analyzable amounts of stable fission products. The simultaneous irradiation of a third foil in a higher flux is therefore necessary, with care taken to ensure that the flux is highly thermalized. Both the 50-mg foil and the highly irradiated foil will be chemically treated alike and selected fission products will be radiochemically determined to establish the ratio of fissions. The fissions in the 50-mg foil will be computed as the multiplied product of the fissionable isotope abundance ratio of the 50-mg foil to the 5- μ g foil and the recorded fissions in the 5- μ g foil. The fissionable isotope abundances will be determined by isotope dilution mass spectrometry.

Capsule Irradiations. A series of irradiations has been readied for U²³³, U²³⁵, Pu²³⁹, and Pu²⁴¹ such that each isotope will be irradiated in graded exposures to depletions ranging from 7 to 50%. Enriched isotopes, as the oxides, have been ordered from ORNL with per cent of major isotope greater than 99 for the first three and greater than 95 for the Pu²⁴¹. The selected irradiation position in the MTR will give a ϕ of $\sim 6 \times 10^{13}$ n-sec⁻¹-cm⁻² with the epicaldium contribution less than 4%.

The irradiation capsules are made of 99.999% aluminum. The respective fissionable nuclide oxides will be mixed with 99.99% aluminum powder, which is necessary for heat conduction. The amount of fissionable

nuclide in each capsule is to vary from 50 mg for the longest irradiation to ~ 100 mg for the shortest. Milligram amounts of stable fission product nuclides will be produced in these irradiations. The pre-irradiation amount of the fissionable isotope in each capsule will be determined by isotope dilution mass spectrometry to 1% standard deviation or better. After irradiation, each capsule will be entirely dissolved and the remaining fissionable isotope content will be determined, also by isotope dilution mass spectrometry. From mass balance equations, the number of fissions should be computable to better than 2% standard deviation.

The aluminum materials have been analyzed by neutron activation. Only trace impurities of lanthanum, scandium, and terbium were observed, less than can significantly affect the fission product yields.

The purpose of the series of graded exposures is twofold; to provide multiplicate samples to increase the validity of the data, and to verify the usefulness of certain relationships proposed for burnup based on the buildup and depletion of selected fission product nuclides as a function of ϕ and exposure time.

FAST ENERGY REGION

A series of aluminum capsules, containing the fissionable nuclide materials summarized in Table I, was irradiated in EBR I.

TABLE I. FISSIONABLE NUCLIDES IRRADIATED IN EBR I

<u>Major Isotope</u>	<u>Enrichment, %</u>	<u>Chemical Form and Amount</u>
Th^{232}	Natural, 100	Metal, 91.1 mg
U^{233}	99.2	U_3O_8 , 82.8 and 96.5 mg (2 capsules)
U^{238}	99.94	U_3O_8 , 100 mg
Pu^{239}	99.97	PuO_2 , 65.0 mg
Pu^{240}	98.0	PuO_2 , 43.2 mg
Pu^{241}	93.3	PuO_2 , 6.7 mg

The mean neutron energy of this reactor is ~ 400 kev peaked at ~ 100 kev which essentially is a pure fission spectrum. Fission yield data obtained from this reactor would represent the maximum, in terms of neutron energy, for reactors.

Due to a shutdown of the EBR I, the irradiation exposure was less than desired. The depletion of the fissionable isotopes was less than 0.05% so that an independent measure of per cent fission by the change in the ratios of heavy element isotopes, based on pre- and post-irradiation mass spectrometer analyses, is not possible. Hence, any fission yield data will necessarily be relative. It is hoped that another fast reactor with in-pile irradiation facilities can be located in the future to establish absolute yields.

MEASUREMENT OF CROSS SECTIONS

About 50 enriched, stable isotopes in the range of the fission products have been obtained. These are being irradiated, bare and cadmium covered, to establish the thermal and epicadmium cross sections. In most cases, the $A + 1$ nuclide also is stable requiring mass spectrometry analysis for the measurement.

Data have been obtained for Pd^{106} . The calculated cross sections were $\sigma_{\text{th}} = 0.3\text{b}$ and $\sigma_{\text{epi}} = 6.5\text{b}$. An apparent high cross section for Pd^{105} , a major isotopic impurity in the starting material, somewhat clouds these values and confirming experiments are planned.

ANALYTICAL METHODS FOR FISSION PRODUCTS

MASS SPECTROMETRY

Mass spectrometry, the principal analysis technique in this project, is used extensively in the programs of fission yield and cross section measurements, and for the measurement of the depletion of fissionable isotopes irradiated for burnup standards.

The two-stage, triple-filament mass spectrometer, manufactured by Nuclide Analysis Associates, was received in June, 3 months behind schedule. Satisfactory operation had not been obtained by the end of the year. The major instrumentation difficulties have been:

1. The pulse counting system has an apparent loss of 45% at 100 kc. in a 100-mc. system.
2. The electrometer measurement of the electronmultiplier output is extremely noisy.
3. There have been transistor failures in the d.c.-filament power supply due to overheating. This has been partially remedied by the addition of blowers.
4. The support for the electrometer collector cup, located between the second stage and the electron multiplier, was found to be broken with the cup partially covering the slit. This required venting and dismantling of the instrument for the necessary repair.

5. Wiring had to be replaced due to overheating, once caused by a loose connection to an ammeter in the power control section and at another time by contact with a high wattage resistor.
6. A ball has been replaced in a vacuum valve between the source and slit. The leak has been only partially eliminated.

SEPARATION METHODS FOR STABLE FISSION PRODUCTS

In the development of separation methods, which are required for the determination of fission yields in the series of capsule irradiations, the underlying base is applicability to various types of reactor fuels. Thus the methods will have future worth for the determination of burnup on actual fuel samples.

Lanthanides. For the chromatographic separation of the lanthanides, the method of Smith and Hoffman⁽⁴⁾ has proven efficient. The column is Dowex 50, X4 (325-400) mesh and the elutant is 0.5M α -hydroxyisobutyric acid at pH 3.3 to 3.9. Stable samarium and neodymium fractions have been separated from 5-month cooled fission products.

An automatic collection apparatus has been fabricated for chromatographic separations. The column effluent passes through a flowthrough type of scintillation crystal which is coupled by a rate meter to a strip chart recorder. This eliminates the usual collection of small incremental volumes as the optimum separation points are indicated by the valleys between activity peaks. High-purity tracers can be added to locate desired fractions.

Chemical separations precede the chromatographic column to separate the lanthanides above cerium from other fission products, from the transuranics, and from cerium. The separation from cerium is desirable because cerium-144 and its Pr-144 daughter contribute more than 95% of the total gamma activity of the lanthanide group for aged fission products. The procedure that is being investigated consists of a double hydroxide precipitation, passage through a column of a mixture of nitrate-form anion exchange resin and lead dioxide, and a fluoride precipitation from a dilute nitric acid-peroxydisulfate medium. In the column, the lead dioxide oxidizes cerium to the +4 valence state which is retained on the anion exchange resin as a negative nitrate complex. Also held on the resin are uranium, neptunium, and plutonium. In the fluoride precipitation, americium remains soluble as a hexavalent fluoride complex.⁽⁵⁾

This procedure has given satisfactory decontamination of all activities except zirconium. The addition of zirconium holdback carrier, in the fluoride precipitation step, is being tried.

Palladium. A method has been developed for the carrier-free separation of palladium. Palladium is extracted as the dimethylglyoxime complex into chloroform from 0.3M hydrochloric acid saturated with oxalic acid, then is backextracted with 8M ammonium hydroxide. Clean separations with excellent decontamination of all fission products have been obtained on metal-uranium alloy fuels including stainless steel.

Inert Gases. Stable isotopes of krypton and xenon are promising burnup monitors, including the ratio approach discussed in the later section "Usefulness of Ratios of Fission Product Nuclides of the Same Element for Burnup Determination."

A collection system⁽⁶⁾ was adapted for the recovery of these gases from the off-gas produced during the dissolution of irradiated fuel. After passage through 0.2M potassium permanganate, 10M sodium hydroxide, and anhydrous manganese perchlorate, the inert gases were collected on a 16-inch, -40 +50 mesh, charcoal column in a copper U tube. The column was kept at -80°C in a dry ice-acetone bath.

Samples collected from an irradiated U²³⁵-aluminum fuel specimen were analyzed by mass spectrometry. High amounts of N₂O, 100 to 1 mole ratio to the inert gases, hindered the analysis. Modifications to the collection system are being investigated to remove or decompose the N₂O.

SEPARATION METHODS FOR RADIOACTIVE FISSION PRODUCTS

Only two radioactive fission products, Sr⁹⁰ and Cs¹³⁷, have sufficiently long half lives for use as fission monitors for long-residence reactor fuels.

Strontium-90. The effort to develop a highly reliable method for the radiochemical determination of Sr⁹⁰ was continued on a limited scale. The proposed method is based on the separation and 4 π β counting of the 64-hr Y⁹⁰ daughter because of its higher beta energy and preparation of a weightless source.

Strontium first is separated from gross fission products by precipitation as the nitrate. It is then adsorbed onto a Dowex 50, X8, column from a pH 5.2, 0.5% ammonium citrate medium. Yttrium-90 is eluted with this same medium. After a measured time interval, the grown-in Y⁹⁰ is eluted, ignited to destroy all organic matter, and mounted on VYNS film for counting. Recoveries of known amounts of Y⁹⁰, added as an IAEA standard, were within 2%. However, there was noticeable amounts of solids on the film which may have caused significant self absorption.

Cesium-137. Due to a concern with the validity of commercially-supplied Cs^{137} standards, a program had been initiated to prepare Cs^{137} effectively free of Cs^{134} .

An enriched, 56% Xe^{136} sample was obtained from the Mound Laboratory. Based on a computer calculation to obtain a maximum $\text{Cs}^{137}/\text{Cs}^{134}$ ratio, of 1600, for the Xe^{136} - Xe^{132} isotopic content of this sample, the sample was irradiated for 60 hours at a thermal flux of 1×10^{14} n-cm⁻²-sec⁻¹. A gamma scan analysis of the irradiated sample showed no detectable Cs^{134} .

About this time, Nuclear Chicago made available a Cs^{137} standard, designation ASTM, with a standardization based on mass analysis by the Vallecitos Laboratory and ion chamber measurement by the National Bureau of Standards. Measurements on this standard here and by other laboratories involved with the ASTM Burnup Task Force have indicated a high degree of confidence with the assigned standardization value. For this reason, no further work is planned with the irradiated sample.

FISSION YIELD COMPILATIONS OF VARIOUS FISSION PRODUCTS FOR BURNUP MONITORS

The literature has been reviewed for fission yield data for fissionable isotopes Th^{232} , U^{233} , U^{235} , U^{238} , Pu^{239} , Pu^{240} , and Pu^{241} as a function of neutron energy. Stress has been placed on data reported since 1959, the last Katcoff⁽⁷⁾ summary.

Weaver, Strom, and Killeen⁽⁸⁾ recently have tabulated total chain yields and independent fission yields, based both on theoretical considerations and on Katcoff's reported data, for fission and 14-mev neutrons for U^{233} , U^{235} , U^{238} , and Pu^{239} , and for thermal neutrons for U^{233} , U^{235} , and Pu^{239} . Using these data, fission yields were plotted as functions of neutron energy and of fissioning isotope (Figures 1 through 6). These plots can serve as guides to predict the usefulness of selected fission products for various burnup determinations.

An example of usefulness is shown by a consideration of Figures 1 and 4. According to Figure 4, the difference in the fission yields of U^{235} and Pu^{239} is greatest in the mass region 105 to 116. Thus this region appears best for differentiating the relative fissions in a fuel in which U^{235} and Pu^{239} are contributing the bulk of the fissions. However, in Figure 1, the fission yields of U^{235} are seen to be highly dependent on neutron energy in this same mass region. Hence, the neutron spectrum to which the sample has been exposed would have to be well known.

Figure 1. Fission Yield Ratio $\frac{\text{U}^{235} \text{ Fission Neutrons}}{\text{U}^{235} \text{ Thermal Neutrons}}$

CPP-S-3091

Figure 2. Fission Yield Ratio $\frac{^{233}\text{U Fission Neutrons}}{^{233}\text{U Thermal Neutrons}}$

CPP-S-3092

CPP-S-3089

Figure 3. Fission Yield Ratio $\frac{\text{Pu}^{239} \text{ Fission Neutrons}}{\text{Pu}^{239} \text{ Thermal Neutrons}}$

Figure 4. Fission Yield Ratio $\frac{\text{Pu}^{239} \text{ Thermal Neutrons}}{\text{U}^{235} \text{ Thermal Neutrons}}$

Figure 5. Fission Yield Ratio $\frac{\text{Pu}^{239} \text{ Fission Neutrons}}{\text{U}^{235} \text{ Fission Neutrons}}$

Figure 6. Fission Yield Ratio $\frac{\text{Pu}^{239} \text{ Fission Neutrons}}{\text{U}^{238} \text{ Fission Neutrons}}$

USEFULNESS OF RATIOS OF FISSION PRODUCT NUCLIDES OF THE SAME ELEMENT FOR BURNUP DETERMINATION

In the past, computer calculations have been made for the buildup and burnout of many fission product nuclides, mainly for U^{235} with literature-reported thermal neutron constants. Input variables were flux levels and exposure times. The purpose was to estimate the effect of ν and t on parasitic neutron captures which causes non-linearity between the number of atoms of a fission product nuclide and the number of fissions.

From these data, a new approach for burnup analysis was indicated; the use of the ratio of two stable fission product nuclides of the same element. The basis is that one nuclide has a high cross section and is depleted by capture while the other has essentially zero cross section. Thus the ratio of the atoms changes with irradiation exposure, which in turn might be relatable to fissions.

This approach would minimize three major disadvantages of the currently-used technique of measuring the abundance of a fission product nuclide and computing the fission by dividing by its fission yield.

1. An absolute atom abundance measurement is not required; only an isotopic ratio is determined.
2. Volume measurements, difficult to do with highly radioactive samples, are not required.
3. Complete sample dissolution, while desirable, is not mandatory because only the isotopic composition of a selected fission product element is measured.

Isotope pairs of xenon, krypton, and neodymium are being investigated for usefulness. A separate report is planned for publication.

The series of capsule irradiations (see section "Measurement of Fission Yields-Capsule Irradiations") will provide samples with varying levels of burnup to experimentally evaluate this approach.

UNCERTAINTIES IN DEPLETION ESTIMATES

In fuel fabrication, there is considerable blending and reworking. As a result, there is considerable uncertainty in the isotopic composition of the uranium, especially in the U^{236}/U^{235} ratio. For this reason, a primary goal of this program is the development of methods which do not require an accurate knowledge of preirradiation composition. In fact, the ideal method would be based solely on postirradiation analyses. Two burnup measurements are desired; (1) the number of fissions produced, both total and the relative contribution from each fissioning isotope, and (2) the degree of depletion of each fissioning isotope.

The determination of fissions appears more straightforward by analyzing for selected fission products. Depletion can be related to fission through the use of alpha, the ratio of the capture cross section to the fission cross section of a nuclide. Alpha and depletion can be computed with input information of fissions, preirradiation isotopic composition, and postirradiation isotopic composition.

To gain some feeling for the magnitude of the error contributed by using preirradiation isotopic composition with large uncertainties, errors were propagated for commonly used formulas for the determination of alpha and of depletion of U^{235} . The data are summarized in Table 2.

The input information consisted of:

1. The sample was a thin foil of 93% U^{235} and was irradiated to 27% depletion of the U^{235} .
2. An independent determination of fissions had been made at a selected level of precision.
3. The precision values that were used for the postirradiation analyses for the uranium isotopic compositions were actual laboratory quality control data.
4. Uncertainty levels were assumed for the preirradiated uranium isotopic composition with especially large uncertainties in the U^{236} fraction.

It is observed that the uncertainties in alpha and depletion are relatively independent of the large uncertainties in pre U^{236} abundance compared to the contribution from the independent determination of fissions. The overall conclusion is that fuel fabricators, by supplying isotopic composition data of the preirradiated fuel, can provide the means to calculate fairly precise depletion of U^{235} in high-enrichment fuel.

DISSOLUTION STUDIES OF IRRADIATED FUELS

Chemical analysis methods for burnup based on fission product determinations, except the ratio approach discussed previously, require complete recovery of the fission products from the irradiated specimens. Dissolution of samples without loss of the analyzed-for fission products is therefore necessary.

Acid dissolution methods were investigated for uranium metal and three types of uranium alloy fuels, uranium-aluminum, uranium-Zircaloy, and UO_2 -stainless steel. To establish completeness of fission product recovery, the three nuclides Zr^{97} , Mo^{99} , and Ce^{143} were determined. These were selected on the basis of their divergent chemical behavior.

TABLE 2. UNCERTAINTIES IN DEPLETION ESTIMATES

Case	Precision, As Standard Deviation									
	Input Data						Output Data			
	Pre U ²³⁵		Pre U ²³⁶		Fissions		Alpha		Depletion U ²³⁵	
	Atom Fraction	%	Atom Fraction	%	Atom Fraction	%	Absolute Units	%	Atom Fraction	%
1	0.001	0.11	0.001	50	0.01	4.5	0.001	6.5	0.010	3.7
2	0.001	0.11	0.0004	20	0.01	4.5	0.010	6.0	0.010	3.7
3	0.001	0.11	0.0004	20	0.002186	1.0	0.0029	1.7	0.0023	0.8

URANIUM METAL AND URANIUM-ALUMINUM ALLOYS

Of the many acid mixtures studied, chloride-rich aqua regia gave the only consistent recovery of the three nuclides. A series of irradiated specimens was dissolved with the aqua regia mixture with variables of added fluoride and of carriers of zirconium, molybdenum, and cerium. Fluoride was studied because it accelerated the rate of dissolution, particularly for the uranium-aluminum samples. The data are summarized in Table 3 as the obtained Zr^{97} , Mo^{99} , and Ce^{143} ratios as a function of these variables.

TABLE 3. RATIOS OF Zr^{97} , Mo^{99} , and Ce^{143} IN AQUA REGIA DISSOLVED URANIUM AND URANIUM-ALUMINUM FUEL SPECIMENS

Variable	Ratios		
	Mo^{99}/Ce^{143}	Mo^{99}/Zr^{97}	Ce^{143}/Zr^{97}
1. U^{235} metal	1.049	1.208	1.158
U^{235} -Al alloy	1.021	1.155	1.139
2. With Zr, Mo, Ce carriers	1.033	1.176	1.139
Without Zr, Mo, Ce carriers	1.028	1.222	1.184
3. With fluoride added	1.031	1.179	1.149
Without fluoride added	1.039	1.198	1.154
Grand average of 11 irradiations	1.036	1.184	1.147
Literature value, based on thermal fission yield values for U^{235} .	1.01	1.03	1.02

The experimental Mo^{99}/Ce^{143} ratios agree closely with the literature value which indicates that full recovery of these nuclides was obtained. Also this ratio was not affected by either the addition of carriers or of fluoride.

On the other hand, the experimental Mo^{99}/Zr^{97} and Ce^{143}/Zr^{97} ratios disagree with the literature values by 15%. Three possible causes are (1) the recovery of Zr^{97} was low, (2) the literature-reported nuclear constants for Zr^{97} , used to compute the atoms from the measured

disintegration rate, are erroneous, and (3) the literature value for the fission yield of Zr^{97} is high. A low recovery of 15% seems improbable because the precision of the radiozirconium analyses, based on multiplicate samples, was better than 3% standard deviation, and because the effect of the addition of fluoride was insignificant. Because the nuclear constants of the half-life and decay scheme are well known, this leaves a high fission yield value for Zr^{97} as the likely cause. Assuming that the literature yield value is for the chain, a significant independent yield of Nb^{97} is indicated.

One variable that did affect the Mo^{99}/Zr^{97} and Ce^{143}/Zr^{97} ratios was the addition of carriers. With carriers present, the ratios decreased by about 4%. This is attributed to an increased recovery of the Zr^{97} .

The conclusions of this study, for the dissolution of uranium metal and uranium-aluminum alloy, are:

1. Chloride-rich aqua regia is a satisfactory dissolvent.
2. Molybdenum-99 and Ce^{143} are suitable radionuclides for analysis to establish that complete dissolution of samples is obtained. The fission yield ratio value of Mo^{99}/Ce^{143} is 1.036.
3. The addition of fluoride has no effect on this ratio. Hence, it may be used to increase dissolution rates.
4. The addition of microgram levels of carriers is recommended.

URANIUM-ZIRCALOY ALLOYS

A mixture of 5M hydrofluoric acid-2M nitric acid rapidly dissolved, without heat, unirradiated fuel specimens of a uranium-Zircaloy alloy. The dissolution of irradiated specimens was complete with this acid mixture but was about four times slower than for unirradiated material. Heating also was required to maintain the dissolution.

Six irradiated samples were analyzed in duplicate for Mo^{99} and Ce^{143} . The resultant Mo^{99}/Ce^{143} ratio was 1.035 ± 0.006 . This agrees with the value of 1.036 previously obtained for the uranium-aluminum alloys.

URANIUM DIOXIDE-STAINLESS STEEL ALLOYS

Unirradiated fuel samples of UO_2 -stainless steel rapidly dissolved with a 6M nitric-4M hydrochloric acid mixture. However, when samples were irradiated to a total of 3×10^{12} fissions in a period of a few minutes, not one dissolved completely even with long contact at boiling temperature. Also with another series of samples, irradiated to the same nvt level but at lower fluxes for longer time periods, not one was dissolved.

The samples had been prepared for irradiation by flame sealing them in quartz ampoules. Surface passivity, caused by heating from the sealing, was suspected as the cause of nondissolution. This was investigated by sealing some samples in the usual manner and by immersing some of the ampoules in a cooling bath during sealing, then attempting dissolution of both types without any irradiation. Those that had been immersed in the coolant dissolved as readily as untreated samples while those sealed in the usual manner resisted dissolution much like the irradiated samples. A series of "cold-sealed" samples then was irradiated. Dissolution again was slow and incomplete. This indicates that fission heating can cause resistance to dissolution.

In earlier irradiations of uranium-aluminum alloy samples sealed in quartz ampoules, a high degree of discoloration and melting at high fission rates had been observed. An improved packaging technique, in which these samples were packed in fine aluminum powder inside of a welded aluminum capsule for improved heat transfer, resulted in no discoloration nor melting. This technique will be evaluated with the UO₂-stainless steel samples.

STORAGE STABILITY OF DISSOLVED FUEL SAMPLES

Equally important as the complete dissolution of irradiated fuel samples is the stability of the dissolved fission products in storage. In a previous study⁽⁹⁾, the adsorption of fission product solutions onto the storage vessel walls has been described as a function of acid media and vessel materials. This study was extended to Teflon vessels which recently have been marketed.

Fission products, aged about 4 months, were placed in 1M and in 6M nitric acid, and in 50% aqua regia in Teflon bottles. After 11 days, the bottles were emptied and rinsed well with water. The greatest adsorption was from 6M nitric acid, equivalent to ~1% of the gross fission products. The adsorption was nonselective, based on a gamma spectrum of the gross fission product mixture.

From the 1M nitric acid and the 50% aqua regia, radiocerium was the most prominent activity adsorbed. This might be caused by an attraction to the fluoride of the Teflon.

REFERENCES

1. Rein, J. E., Rider, B. F., Burnup Determination of Nuclear Fuels (Progress Report - Calendar Year 1962), TID-17385 (January 1963).
2. Rider, B. F., et. al., Accurate Nuclear Fuel Burnup Analysis, Quarterly Progress Reports for Period December 1, 1961 to November 30, 1963, GEAP-4053-1, GEAP-4053-2, GEAP-4137, GEAP-4201, GEAP-4278, GEAP-4361 and GEAP-4430.
3. Shank, R. C., Annual Report of Division Analytical Branch for 1963, IDO-14636, pp. 49-69 (June 1964).
4. Smith, L., Hoffman, D. C. "Ion Exchange Separations of the Lanthanides and Actinides: Elution with Ammonium Alpha-Hydroxy-Isobutyrate", J. Inorg. Nucl. Chem. 3, 243 (1956).
5. Moore, F. L. "Separation of Americium from other Elements", Anal. Chem. 35, 715 (1963).
6. Koch, R. C., Grandy, G. L. "Rapid Method for Separation and Analysis of Radioactive Fission Gases", Anal. Chem. 33, 43 (1961).
7. Katcoff, S. "Fission Product Yields From Neutron-Induced Fission" Nucleonics 18, No. 11 201 (1960).
8. Weaver, L. E., Strom, P. O., Killeen, P. A. Estimated Total Chain and Independent Fission Yields for Several Neutron-Induced Fission Processes, USNRDL-Tr-633 (1963).
9. Maeck, W. J., Rein, J. E., "Storage of Radioactive Fission Product Solutions", Anal. Chem. 36, 252 (1964).

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION