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FISSION PRODUCT CALCULATIONS AND MEASUREMENTS IN HIGHLY IRRADIATED, HIGHLY ENRICHED URANIUM

W. C. PERKINS
R. P. CHRISTMAN

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Savannah River Laboratory

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FISSION PRODUCT CALCULATIONS AND MEASUREMENTS IN HIGHLY IRRADIATED, HIGHLY ENRICHED URANIUM

by

W. C. Perkins

R. P. Christman

Approved by

E. L. Albenesius, Research Manager
Separations Chemistry Division

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E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, S. C. 29801

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ABSTRACT

The CINDER computer program is a valuable tool for calculating fission product activities in nuclear reactor fuel and targets. CINDER predicts the activities of ^{103}Ru, ^{106}Ru, ^{134}Cs, ^{137}Cs, and ^{144}Ce within an average standard deviation of 19%. However, only 10% of the ^{95}Nb and 68% of the ^{95}Zr predicted by CINDER were found in solutions of irradiated enriched uranium. Large amounts of ^{95}Nb and some ^{95}Zr were found in the colloidal, siliceous solids that form during dissolution of this fuel. The $^{95}Nb/^{95}Zr$ ratios measured in solution indicate that almost all of the ^{95}Nb had been removed from solution by these solids at the time the fuel was dissolved.

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INTRODUCTION

Computers have been used to calculate fission product activities in spent nuclear fuel for a number of years. These calculations can determine fission product poisoning in nuclear fuel, thermal cooling requirements of irradiated fuel elements, and the decay time necessary before beginning chemical processing.

This report includes several new aspects of the continuing effort to improve the accuracy of computer-predicted fission product activities. The CINDER computer program, first developed by T. R. England,[1-3] has been revised and converted to FORTRAN IV language for use at Savannah River Laboratory. A second program, HAMMER,[4] is used to obtain much of the CINDER input, such as cross section and flux data.

A major objective of the work described in this report was to measure the accuracy of CINDER predictions for highly irradiated, highly enriched uranium. The burnup of ^{235}U in the fuels analyzed in this report are among the highest ever attained for ^{235}U fuel of high enrichment; fission product activities had not previously been evaluated for such conditions. Calculation techniques used at low ^{235}U burnup are inadequate at high ^{235}U burnup because neither fuel depletion nor neutron captures in fission products are considered.

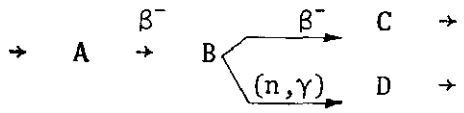
A third computer program, GELI-SPAN,[5] was used to analyze the gamma ray data from test samples. The use of high-resolution solid-state gamma ray detectors improved the accuracy of measurement of specific fission products and helped explain a discrepancy between predicted and measured ^{95}Nb activities.

DESCRIPTION OF CINDER

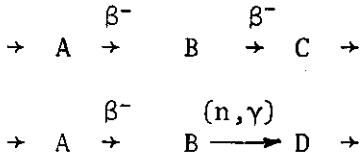
CINDER is a computer program that calculates the time-dependent concentrations of isotopes coupled through radioactive decay chains and neutron absorption processes. This program is applicable for the solution of any problem in which the isotope coupling can be expressed in linear differential equations. CINDER is particularly useful in calculating fission product activities in highly irradiated fuels, because provisions are made for fuel depletion, for neutron activation of stable fission products, and for flux variations during the irradiation period.

CINDER requires a set of two cross sections for each fission product and four cross sections for each fuel. Each cross section is applied to a portion of the neutron energy spectrum; for example, Group 4 is the thermal group, 0 to 0.625 eV. These cross sections can be obtained from the HAMMER[4] code. Further details are given in the Appendix (p. 15). A compilation of the ^{235}U fission yields and fission product decay constants used in CINDER is also given in the Appendix.

The production chains for many fission products are branched. The CINDER program resolves such a chain into several unbranched subchains; each chain is described by a linear differential equation. For example:



can be resolved into:



CINDER solves the coupled linear differential equations for fission product concentrations in each chain. The concentration of an isotope produced by several chains is found by summing the contributions from each chain. Currently, approximately 190 different fission products are represented as 362 isotopes in 67 unbranched chains. Nuclides with half-lives less than four hours are not included in the chains.

CINDER is particularly applicable to long-term irradiations where reactor power is not constant. About 100 time steps can be used. Each time step represents an irradiation period at a different flux or a cooling period at zero flux. Times as short as 2 hours have been used for periods with zero flux to simulate actual shutdowns during reactor operation.

COMPARISON OF PREDICTED AND MEASURED ACTIVITIES

After discharge from a nuclear reactor, fuel elements are cooled for a time to allow decay of fission products before chemical processing begins. In this study, because cooling times were in the range of 3 to 6 months, only the fission products with half-lives longer than 1 month could be measured accurately; however, only these fission products influence fuel reprocessing operations significantly. Enriched uranium fuels that had been irradiated in three different SRP reactor campaigns were analyzed for long-lived fission products. A comparison of the results with CINDER predictions is shown in Table I. In these calculations, CINDER used the actual reactor conditions for each campaign, including flux values measured in the reactor core.

TABLE I

Accuracy of CINDER Predictions

Sample	I	II	III
Days Cooled:	180	180	94
	Ratio, Measured Activity/Calculated Activity		
^{95}Zr	0.56	0.86	0.63
^{95}Nb	0.16	0.11	0.043
^{103}Ru	0.84	1.01	0.69
^{106}Ru	1.20	1.13	0.73
^{134}Cs	0.69	0.99	1.11
^{137}Cs	1.24	1.26	1.03
^{144}Ce	1.04	1.03	0.87

CINDER predictions for Ru, Cs, and Ce isotopes agreed well with the measured activities. The average of their ratios in Table I is 0.99 ±0.19. The ability of CINDER to predict ^{134}Cs activity is particularly important because this isotope is not a true fission product, but the product of neutron capture in a stable fission product, ^{133}Cs. The agreement between measured and predicted values for ^{95}Zr was fair (average ratio, 0.68); measured values for ^{95}Nb were much lower than predicted (average ratio, 0.10).

Fission Product Analysis

Fission product activities were measured after the irradiated fuel assemblies were dissolved in nitric acid solutions containing $Hg(NO_3)_2$. A high-resolution, lithium-drifted germanium detector coupled to a 4096-channel pulse height analyzer was used to measure the gamma ray spectra from the solutions. A data analysis computer code, GELI-SPAN,[5] identified the nuclides contributing to the spectrum, analyzed statistical counting errors, and reported the activity of each nuclide detected.

Samples from three different reactor campaigns at the Savannah River Plant were analyzed to test the predictions of the computer code. The ^{235}U burnup in each campaign was different. Samples I and II were taken from process dissolver solutions; Sample III was obtained by cutting a small segment from the middle of a fuel tube.

The Special Case of ^{95}Nb

The rather large discrepancy between measured and predicted ^{95}Nb activities and the generally accurate predictions for other fission products indicated that most of the ^{95}Nb was not present in the test solutions. Previous experience at Savannah River showed that $^{95}Zr + {}^{95}Nb$ activities in process solutions were routinely lower than predicted, but $^{95}Nb/^{95}Zr$ ratios were not routinely measured.

The ^{95}Nb discrepancy is caused by efficient scavenging of ^{95}Nb from solution by the siliceous solids that form whenever high-burnup U-Al alloy fuels are dissolved. Solids centrifuged from solutions of dissolved fuel contained silicon as the major cationic constituent and aluminum as a minor constituent; 82% of the gamma activity in these solids was due to ^{95}Nb (Table II). The $^{95}Nb/^{95}Zr$ ratio (12) in these solids was significantly greater than the secular equilibrium value of 2.17 that represents the theoretical maximum for this ratio in the absence of a chemical separation.

In the solutions from which the solids had been removed, the $^{95}Nb/^{95}Zr$ activity ratios were all less than 2.17. The $^{95}Nb/^{95}Zr$ ratios measured in these solutions could not be correlated to the cooling time of the irradiated fuel. However, there was a correlation between these ratios and the time elapsed since the fuel was dissolved, if ^{95}Nb was assumed to be completely scavenged from solution by the dissolver solids. The measured ratios in solution are compared to the theoretical curve for the approach of ^{95}Zr-^{95}Nb to secular equilibrium in Figure 1. The correlation is good only for samples that had been centrifuged to remove the dissolver solids because the solids continue to partially scavenge ^{95}Nb as it forms from the decay of ^{95}Zr.

TABLE II

Fission Products in Undissolved Solids

	Gamma Activity, % of total
^{95}Nb	82
^{95}Zr	7
^{144}Ce	6
$^{103}Ru + ^{106}Ru$	3
$^{134}Cs + ^{137}Cs$	2

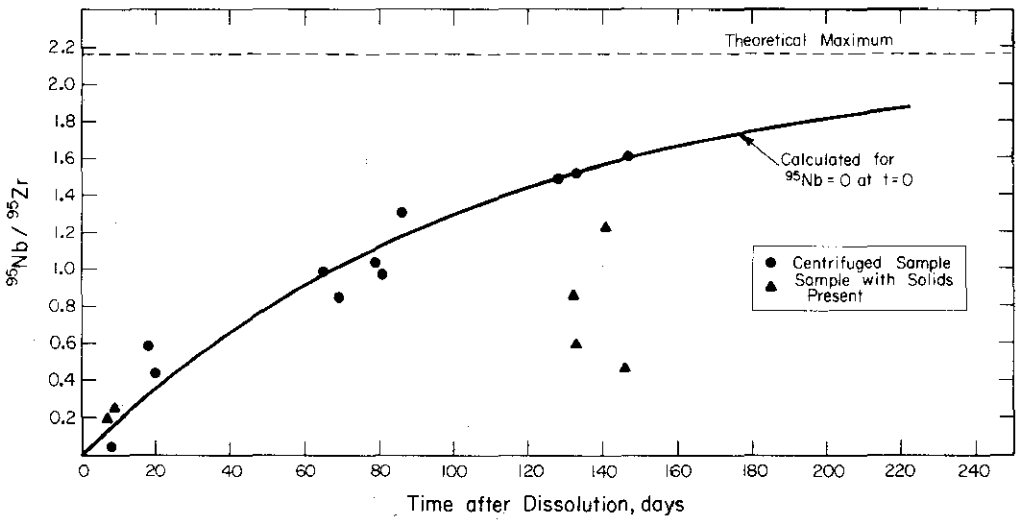


FIG. 1 COMPARISON OF MEASURED $^{95}Nb/^{95}Zr$ ACTIVITY RATIOS TO THEORETICAL CURVE

As further evidence of ^{95}Nb scavenging in the Savannah River Plant process, almost one million curies of ^{95}Nb were found in the plant dissolver after the highly irradiated fuel was processed. Moreover, the only other gamma activity found was ^{95}Zr, as shown in Table III. No quantitative comparison was made between the amount of ^{95}Nb removed in these flushes and the amount missing according to the CINDER predictions, because the complexity of operations did not allow accurate calculation and because all the ^{95}Nb may not have been removed from the dissolver. However, the quantity of ^{95}Nb found indicates that ^{95}Nb was efficiently scavenged from solution during fuel dissolution. The average $^{95}Nb/^{95}Zr$ ratio for the two flush solutions (2.5) is significantly greater than the equilibrium ratio of 2.17, considering that flushing operations began about two ^{95}Nb half-lives (70 days) after dissolving operations began and that ^{95}Zr decays more slowly ($t_{1/2}$ = 65 days).

TABLE III

Fission Product Activity in Process Dissolver Flushes

Relative Volume	Flush Composition	Gamma Activity Removed		
		Relative	% ^{95}Nb	% ^{95}Zr
100	1M HNO_3	1.0	*a*	*a*
108	3M HNO_3	4.2	81	19
218	7M HNO_3-0.025M HF-0.12M $Al(NO_3)_3$	13.6	68	32

a Not analyzed

The behavior of ^{95}Nb in dissolved fuels is not due to the low solubility of niobium in acid solutions; in 2 to 9 M HNO_3 the solubility is about 52 ppm.[6] Niobium precipitates from acid solution as a colloidal, hydrated pentoxide; in basic solution it forms niobic acid, an extremely weak acid similar to silicic acid.[7] CINDER predicts that only 5 ppm of ^{95}Nb was present in Savannah River dissolver solutions. Consequently, all of the ^{95}Nb could have dissolved, if it had not been scavenged by the silicon-containing solids.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of Mr. J. Harold Dickson, Separations Technology Section, Savannah River Plant in compiling the process data in Table III.

APPENDIX

CINDER Input Data

CINDER requires a set of four-group cross sections for each fission product and for each fuel. Each set can include thermal values (2200 m/sec), resonance integrals, or spectrum-averaged cross sections. These last values are preferred and can be obtained from HAMMER calculations. If spectrum-averaged cross sections are not available, a set may be generated as follows:

$$\sigma_4 = \sigma_{2200} \cdot g_4$$

$$\sigma_3 = \frac{R}{9.1} \cdot g_3$$

$$\sigma_2 = \frac{R}{5.0}$$

$$\sigma_1 = \frac{R}{2.5}$$

where

R = infinitely dilute resonance integral

g_4 = thermal spectrum index

g_3 = Group 3 shielding factor

The assumptions are that the thermal cross section is proportional to 1/v and that the epithermal flux is proportional to 1/E. The thermal spectrum index is equal to the spectrum-averaged thermal cross section of the HAMMER isotope having the identification 1 (unit 1/v absorber), or the spectrum-averaged cross section of any 1/v absorber divided by its 2200 m/sec cross section. Fuel cross sections are altered with increasing exposure by adjusting the Group 3 and 4 shielding factors. Fission product thermal cross sections can be varied by changing the thermal spectrum index.

CINDER input must also include either a power density or a thermal flux along with the three fast-to-thermal flux ratios. These data can be obtained from HAMMER calculations and from values measured in the reactor. Because CINDER is a point cal-

culation, all input quantities, such as power, must be in terms of that quantity divided by the volume of the assembly.

A CINDER printout includes a listing of input data, along with the fission product library of yields, decay constants, and cross sections. At each time step, fuel concentrations, fission densities, total absorptions, and absolute and integrated fluxes are printed. The fission product information includes optional listing of any isotope's concentration, activity, and macroscopic cross sections in addition to the total activity, and total macroscopic cross sections. A summary for each set of calculations is provided after the last time step.

A compilation of ^{235}U fission yields, decay constants, and cross sections is given in Table IV. CINDER also contains the yield values necessary to calculate fission products from ^{233}U, ^{238}U, ^{239}Pu, ^{241}Pu, ^{244}Cm, and ^{245}Cm.

TABLE IV

Some CINDER ^{235}U Fission Yields and Decay Constants

[Criteria: Yield >0.1% and $t_{1/2}$ >3 days]

	Yield, %	λ, sec^{-1} [a]		Yield, %	λ, sec^{-1}
^{85}Kr	.293	.2072 E-08	^{133}Xe	0	.1522 E-05
^{89}Sr	4.79	.1589 E-06	^{133}Cs	0	0
^{90}Sr	5.77	.7845 E-09	^{134}Cs	0	.9550 E-08
^{94}Zr	6.40	0	^{136}Xe	6.46	0
^{95}Zr	6.20	.1234 E-06	^{137}Cs	6.15	.7471 E-09
^{95}Nb	0	.2292 E-06	^{140}Ba	6.35	.6268 E-06
^{102}Ru	4.10	0	^{140}La	0	.4790 E-05
^{103}Ru	3.00	.2021 E-06	^{141}Ce	6.40	.2431 E-06
^{106}Ru	.380	.2175 E-07	^{143}Ce	6.00	.5385 E-05
^{127}Sb	.102	.2116 E-05	^{144}Ce	5.62	.2865 E-07
^{129m}Te	.350	.2168 E-06	^{147}Nd	2.36	.7228 E-06
^{131}I	2.49	.9966 E-06	^{147}Pm	0	.8289 E-08
^{132}Te	4.38	.2501 E-05	^{151}Pm	.440	.6780 E-05
^{133}I	6.59	.9257 E-05	^{151}Sm	0	.2746 E-09

[a] .2072 E-08 = 0.2072×10^{-8}

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