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Evaluation of High Burnup Fuel Performance\*

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## URANIUM AND PLUTONIUM DETERMINATIONS FOR EVALUATION OF HIGH BURNUP FUEL PERFORMANCE

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### ABSTRACT

The purpose of this work is to experimentally test computational methods being developed for reactor fuel operation. Described are the analytical techniques used in the determination of uranium and plutonium compositions on PWR fuel that has spanned five power cycles, culminating in 55,000 to 57,000 MWd/T burnup. Analyses have been performed on ten samples excised from selected sections of the fuel rods. Hot cell operations required the separation of fuel from cladding and the comminution of the fuel. These tasks were successfully accomplished using a SpectroMil, a ball pestle impact grinding and blending instrument manufactured by Chemplex Industries, Inc., Eastchester, New York. The fuel was dissolved using strong mineral acids and bomb dissolution techniques. Separation of the fuel from fission products was done by solvent (hexone) extraction. Fuel isotopic compositions and assays were determined by the mass spectrometric isotope dilution (MSID) method using NBS standards SRM-993 and SRM-996. Alpha spectrometry was used to determine the  $^{238}\text{Pu}$  composition. Relative correlations of composition with burnup were obtained by gamma-ray spectrometry of selected fission products in the dissolved fuel.

### INTRODUCTION

The change in the isotopic composition of a fuel as a function of burnup is a measure of the irradiation history of that fuel in a power reactor. Mathematical expressions required to describe the operating irradiation history are complex and depend upon detailed knowledge of core configuration, fuel management programs, spatial neutron flux distributions, neutron spectra, and cross section data. Experimental data obtained from LWR spent fuel indicates that there are relationships between isotopic concentrations that have a predictable, functional behavior over a broad range of reactor operating conditions and burnup. These observed functional relationships, when coupled with reactor analysis and computational methods, may be used to optimize the fuel management of a reactor and fuel reprocessing plant and, perhaps more importantly, can be used as an accountability measure for the safeguards of nuclear materials.

The primary objective of this paper is to describe the analytical techniques and methods used in obtaining heavy element isotopic data that will be the basis of a subsequent, more detailed study on the isotope correlation technique. Summarized will be a brief history of the Zion fuel; experimental techniques for the separation of the fuel from cladding; comminution, dissolution, and chemical separations of the fuel; and, finally, the MSID determination of the isotopic composition.

## FUEL HISTORY

The samples from which the analytical results were obtained resided in the Commonwealth Edison Company Zion PWR reactor for a total of five cycles in fuel assemblies C-63 and C-64. These assemblies were irradiated in Zion 1 for cycles 1, 2, and 3; in Zion 2 for cycle 4; and in Zion 1 for cycle 6. This information is conveniently summarized in Table 1 with coordinates so as to perceive the relative positions of the assemblies in the reactor with the aid of the reference matrix, Figure 1.

Table 1. Fuel Assembly Location

Cycle	Unit	Coordinates	
		C-63	C-64
1	Zion 1	C-3	N-13
2	Zion 1	D-7	M-9
3	Zion 1	C-6	N-10
4	Zion 2	E-5	L-11
6	Zion 1	E-5	L-11

The fuel rods were uranium oxide consisting of zone-3 type fuel with an initial composition of 0.03%  $^{234}\text{U}$ , 3.31%  $^{235}\text{U}$ , and 96.66%  $^{238}\text{U}$ . Two samples from five different rods were excised for analytical analysis. Each sample was approximately 7.6 cm long and was taken from a position 33 cm and 154 cm from the bottom of the fuel rod. Specimen identification, location, and coordinates are given in Table 2. Respective positions of fuel rods within the subassembly can be determined using Fig. 1. The fuel burnup spanning these five cycles is estimated to be 55,000 to 57,000 MWD/T.

Table 2. Subassembly Location

Specimen I.D.	Fuel Assembly	Axial Location <sup>a</sup>	Coord.
624-3	C-63	33-41	F-7
624-18	C-63	154-161	
616-3	C-63	33-41	K-4
616-15	C-63	154-161	
699-3	C-63	33-41	L-12
699-16	C-63	154-161	
642-3	C-64	33-41	E-12
642-15	C-64	154-161	
A10-2	C-64	33-41	A-10
A10-8	C-64	154-161	

<sup>a</sup>Centimeters from the bottom.

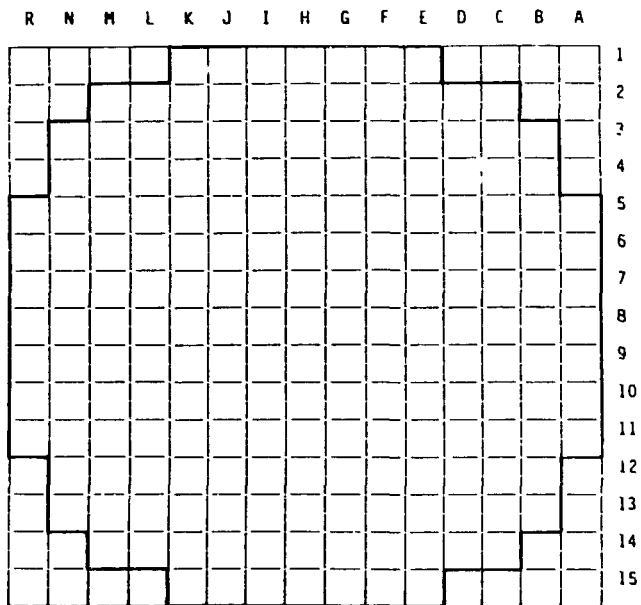


Figure 1. Reference Matrix

## EXPERIMENTAL

### Fuel Sampling

Fuel handling was done in the M-wing hot-cell complex of Building D-200 at Argonne National Laboratory. The hot cell used for the analytical operations on the specimen was a kilo-Curie cell equipped with Model-10 manipulators. An alpha barrier was constructed inside the cell so as to contain all alpha-bearing species and facilitate easy cleanup after operations were completed.

Contained within the alpha barrier were the SpectroMil and SpectroVials (SpectroMil and SpectroVial are U.S. registered trademarks of Chemplex Industries, Inc., 140-T-Marbledale Road, Eastchester, New York) for the comminution of the fuel, a remoted electronic balance for weighing, an oven for the sample dissolutions, and the Parr bomb assembly apparatus.

Each fuel specimen was cut into five pieces approximately 1.5-cm long, and a few of these pieces were placed, along with a grinding ball, into the SpectroVial for removal of the cladding from the fuel. Only a few minutes of comminution were needed for complete separation of the fuel. The cladding pieces were removed and new pieces added to the same vial, and the process was repeated until the entire specimen had been separated from its cladding. At this point another grinding ball was added to the fuel in the vial, and the comminution process continued for about 10 minutes to ensure complete mixing of the entire 50 g of fuel. From this mixed powder, 200-400 mg was taken for the analytical analyses.

Since only a small amount of sample was used for analysis, assurance was needed that the sample taken was indeed representative of the whole. Although the SpectroVial was designed<sup>1</sup> to reduce the sample preparation error for processing powdered samples in ball impact grinders, this fuel sample application had not been demonstrated. Sampling was done on the first powdered specimen, 624-18. Four samples ranging in size from 275 to 565 mg were taken to demonstrate reproducibility. The first two samples were carried through the entire chemical processing; namely, both uranium and plutonium analysis; whereas, with the last two samples, only uranium analyses were performed. On all the samples both heavy element assay and isotopic distributions were determined. Results of this study are given in Tables 3 and 4 and demonstrate good reproducibility among samples.

Table 3. Dry Sampling Reproducibility - Uranium

Specimen I.D.	Sample	Fuel Wt.,						
		mg	U, g/g	233	234	235	236	238
624-18	1	382.6	0.8210	<0.0005	0.0137	0.3827	0.5011	99.102
	2	408.9	0.8214	<0.0005	0.0136	0.3826	0.5008	99.103
			0.8221	<0.0005	0.0138	0.3826	0.5007	99.103
	3	564.6	0.8213	<0.0005	0.0140	0.3843	0.5016	99.100
4	275.3	0.8194	<0.0005	0.0141	0.3835	0.5014	99.101	

Table 4. Dry Sampling Reproducibility - Plutonium

Specimen I.D.	Sample	Fuel Wt., Pu,							
		mg	mg/g	238	239	240	241	242	244
624-18	1	382.6	9.072	3.605	46.532	28.115	11.411	10.335	0.0013
	2	408.9	9.078	3.634	46.497	28.104	11.429	10.335	0.0018

### Fuel Chemistry

Dry powdered fuel samples were weighed in a tared Teflon Parr bomb liner using a remote electronic Mettler AE 160 analytical balance. To the weighed sample 10 mL of conc.  $\text{HNO}_3$ , 0.3 mL conc.  $\text{HCl}$ , and 0.02 mL  $\text{HF}$  were added, the Teflon container was placed in the Parr bomb, and the bomb assembly heated in an oven at  $200^\circ\text{C}$  for approximately 8 hours, which, in all cases, was sufficient time for complete sample dissolution. The cooled solution was then quantitatively transferred to a tared bottle and the net weight of solution recorded. Weighed aliquots were transferred to beakers for subsequent mass spectrometric analysis; only aliquots requiring heavy element assays were transferred to beakers containing  $^{235}\text{U}$  (SRM-993) and  $^{244}\text{Pu}$  (SRM-996) mass spec spikes. Exchange between the spike and the sample is assured by the addition of a small amount of  $\text{HClO}_4$  and  $\text{HF}$  and the solution taken to dryness. This residue is dissolved in 1 N  $\text{HNO}_3$ , the solution transferred to a screw-top bottle

containing methyl isobutyl ketone (hexone) and saturated  $\text{Al}(\text{NO}_3)_3$ . The fuel is extracted into the organic phase from the fission product aqueous phase and the hexone fraction transferred out of the hot cell for subsequent uranium and plutonium separation.

Separation of the plutonium from the uranium was done using concentrated HBr by a method similar to that developed by Larsen<sup>2</sup> and Marsh.<sup>3</sup> The organic phase containing the fuel is stripped into 1 M  $\text{HNO}_3$  and taken to dryness. The residue is dissolved in a small amount of 9 M  $\text{HCl}$ , and this process is repeated twice. The dry residue is redissolved in 9 M  $\text{HCl}$  and loaded onto a preconditioned Hbr anion exchange column (Bio-Rad AG 1 x 8, 100-200 mesh). After a small amount of washing with 9 M  $\text{HCl}$ , the Pu is eluted with 9 M HBr and collected. The U fraction is later eluted with 0.1 M  $\text{HCl}$  and collected separately. Both the Pu and U fractions are taken to dryness and the residues dissolved in concentrated  $\text{HNO}_3$ . The evaporation and conc.  $\text{HNO}_3$  step is repeated twice and the dry residues transferred to the mass spec lab for analysis.

A weighed aliquot from the aqueous phase was removed from the hot cell for the determination of selected fission products.  $^{137}\text{Cs}$  was chosen as the monitor to estimate the fuel burnup. This activity was determined by counting the 0.662 MeV gamma-ray using a calibrated HPGe detector and a 4096-multichannel analyzer.

The isotope  $^{238}\text{Pu}$  was determined by alpha spectrometry. An aliquot from the separated plutonium fraction is electroplated on a stainless steel planchet and the Pu is deposited from a 5%  $\text{NaHSO}_4$  15%  $\text{Na}_2\text{SO}_4$ , water mixture at a current of 1 amp for one hour. This method yields a thin, uniformly distributed plutonium deposit that results in excellent separation of the plutonium isotopes by alpha spectrometry. The ratio of the 238/239+240 peaks are then normalized to the 239+240Pu mass spec results.

## RESULTS AND DISCUSSION

Both the plutonium and the uranium results were obtained with a VG Isotopes 54R mass spectrometer. Summarized in Tables 5 through 8 are the mass spectrometry results for specimens from subassembly C-63 and C-64. All samples were chemically analyzed in duplicate, except for the plutonium results for specimens 642-3 and 642-15. As mentioned earlier, specimen 624-18 was sampled four times to demonstrate sample homogeneity, and this is reflected by the five values given for the uranium content. From these data are demonstrated the excellent agreement between duplicates, both for the uranium and the plutonium.

Table 5. Plutonium Isotopic and Assay Summary

Isotope	C-63					
	624-3	624-18	616-3	616-15	699-3	699-16
238	3.120	3.620	0.561	0.850	2.260	2.694
239	48.602	46.515	71.044	66.092	52.930	49.911
240	27.886	28.110	19.983	22.384	27.078	27.878
241	11.269	11.420	6.472	7.704	10.473	10.773
242	9.122	10.335	1.940	2.971	7.259	8.784
244	<0.001	0.0015	<0.001	-	-	-
mg Pu/g	8.610	9.072	5.423	6.224	7.845	8.273
	8.608	9.078	5.425	6.215	7.852	8.283
Average	8.609	9.075	5.424	6.220	7.849	8.278

Table 6. Uranium Isotopic and Assay Summary

Isotope	C-63					
	624-3	624-18	616-3	616-15	699-3	699-16
233	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
234	0.0150	0.0137	0.0207	0.0188	0.0159	0.0149
235	0.4705	0.3826	1.6418	1.3630	0.6597	0.5304
236	0.4918	0.5009	0.3152	0.3636	0.4674	0.4848
238	99.023	99.103	98.022	98.255	98.857	98.970
g U/g	0.8304	0.8210	0.8550	0.8536	0.8356	0.8318
	0.8300	0.8214	0.8558	0.8533	0.8357	0.8320
		0.8221				
		0.8213				
		0.8194				
Average	0.8302	0.8210	0.8554	0.8535	0.8357	0.8319



Table 7. Plutonium Isotopic and Assay Summary

Isotope	C-64			
	642-3	642-15	A10-2	A10-8
238	1.635	2.042	4.331	4.823
239	57.124	54.120	44.773	42.707
240	25.882	26.643	26.467	26.788
241	9.670	10.163	12.778	12.721
242	5.689	7.032	11.650	12.961
244	<0.001	<0.001	0.0016	<0.01
mg Pu/g	7.313	7.957	9.557 9.529	10.034 10.038
Average			9.543	10.036

Table 8. Uranium Isotopic and Assay Summary

Isotope	C-64			
	642-3	642-15	A10-2	A10-8
233	0.0020	0.0016	0.0002	<0.0005
234	0.0179	0.0161	0.0127	0.0118
235	1.0336	0.7178	0.2874	0.2238
236	0.4387	0.4604	0.5039	0.5077
238	98.508	98.804	99.196	99.257
g U/g	0.8456 0.8438	0.8361 0.8362	0.8178 0.8168	0.8137 0.8130
Average	0.8447	0.8362	0.8173	0.8134

Presented in Table 9 is a correlation of the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  results with estimated fuel burnup. The burnup is considered to be only approximate since exact radiation histories of the two subassemblies were not available at this time. Burnup in atom percent was calculated from the expression,

$$BU = \frac{^{137}\text{Cs}/\text{FY} \times 100}{U + \text{Pu} + ^{137}\text{Cs}/\text{FY}},$$

where FY is the fission yield of  $^{137}\text{Cs}$ . This fission yield was estimated to be about 6.25% since some of the  $^{239}\text{Pu}$  being formed does begin to contribute to the  $^{137}\text{Cs}$  content, especially toward the end of the irradiation. Also, since the determination of fuel burnup was not the primary objective of this study, the correlation using  $^{137}\text{Cs}$  was the most cost effective approach and is presented only as a point of interest. When exact irradiation histories become available, these data will then be the basis for a more detailed and precise correlation study and will encompass all of the measured isotopes.

Table 9.  $^{239},^{240}\text{Pu}$  Versus Burnup (Approximate)

Subassembly	Specimen I.D.	% Burnup (Approx.)	$^{239}\text{Pu}$ , mg/g	$^{240}\text{Pu}$ , mg/g
63	616-3	1.8	3.853	1.085
	616-15	2.2	4.111	1.393
63	699-3	3.9	4.154	2.127
	699-16	4.3	4.132	2.310
63	624-3	4.7	4.184	2.402
	624-18	5.1	4.221	2.550
64	A10-2	5.9	4.273	2.529
	A10-8	6.4	4.286	2.690
64	642-3	3.2	4.177	1.894
	642-15	3.6	4.306	2.117

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