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VII

Determination of Burnup of Fast Reactor Fuels¹

(*R. P. Larsen, R. J. Meyer, C. E. Crouthamel*)

The program for the development of methods for measuring burnup in fast reactor fuels is continuing. To achieve the program's objective it is necessary to

develop accurate analytical methods for determining the concentration of fission products that can be used as burnup monitors and to establish accurate values for their fast fission yields.

¹ A summary of this section is given on pages 14 and 15.

A. EVALUATION OF RARE EARTHS, MOLYBDENUM, AND TECHNETIUM AS BURNUP MONITORS FOR URANIUM OXIDE FUEL (*R. J. Meyer, R. D. Oldham, R. J. Popek*)

A necessary part of developing methods for burnup analysis is the demonstration that a fission product monitor is suitable for a particular type of fuel (e.g., metal, oxide, carbide). The criteria that must be met in selecting a monitor were presented previously (ANL-6900, p. 335). One of the most important of these is that the monitor must be quantitatively retained in the sample for burnup analysis. Both technetium-99 and lanthanum-139 met this criterion for metallic EBR-II fuel. However, in oxide fuels, many fission products are expected to behave differently, and potential monitors for these fuels must be carefully evaluated.

Investigations being performed in a separate program on the chemistry of irradiated fuels (see ANL-7425, pp. 104-113, and this report, Section III.B.2) provided valuable guide lines in the selection of burnup monitors. For example, the studies on the chemistry of irradiated oxide fuels have shown that certain nuclides (e.g., the rare earths) do not appear to migrate during irradiation; therefore, these nuclides are considered excellent candidates for burnup monitors. When extreme migration of a fission product (e.g., cesium) is demonstrated, the nuclide is not a satisfactory monitor. However, for fission products with intermediate degrees of migration (e.g., molybdenum, technetium, ruthenium, barium), the decision is not clear cut, and further investigation is necessary to

establish whether or not a cross-sectional cut of a fuel pin will provide a representative sample of the fission product under consideration.

To clarify the situation with respect to the suitability of molybdenum and technetium as monitors for oxide fuels, a series of analyses was performed on three sections of a 13% enriched UO₂ fuel pin irradiated to ~6 at. % burnup. These sections were 1/8 in. thick and were cut from the top, middle, and bottom portions of the fuel rod. Each section was analyzed for burnup and for uranium, molybdenum, and technetium content. Burnup was determined by pre- and post-irradiation uranium isotopic analysis, and uranium by mass-spectrometric isotopic-dilution analysis. Both molybdenum and technetium were determined spectrophotometrically as their respective thiocyanate complexes after separation from interfering ions by ion exchange and/or solvent extraction. Each of the fuel sections was also analyzed gamma-spectrometrically for ¹⁴⁴Ce (285 days) with a Ge(Li) detector system; the ¹⁴⁴Ce count rate was determined by integration of the photopeak at 134 keV.

The results of the analyses for molybdenum, technetium, ¹⁴⁴Ce, and burnup have been correlated, and these correlations are summarized in Table VII-1. The variations in molybdenum-to-fission and technetium-to-fission ratios in the three sections of the

TABLE VII-1. FISSION PRODUCT-TO-FISSION RATIOS
FOR SECTIONS OF A UO_2 FUEL PIN
(6 AT. % BURNUP)

Sample	Molybdenum- to-Fission Ratio	Technetium- to-Fission Ratio	^{144}Ce Count Rate-to-Fission Ratio
Top	0.209	0.0492	1.66×10^4
Middle	0.242	0.0514	1.66×10^4
Bottom	0.249	0.0528	1.67×10^4

fuel pin indicate that neither molybdenum nor technetium was quantitatively retained in the fuel during irradiation. It is, therefore, concluded that

neither fission product is a satisfactory monitor for oxide fuels. This information is of particular significance because both molybdenum and technetium have been used, or have been considered for use, in other programs for determining burnup in oxide fuels. The good agreement among the cerium-to-fission ratios in the three sections of the fuel pin indicates that cerium was quantitatively retained in the fuel. These data on the behavior of cerium, a typical rare earth, provide further substantiation that the rare earths do not migrate in oxide fuels. Since the rare earths also appear to meet the other selection criteria, they are considered excellent candidates as burnup monitors for oxide fuels.

B. DEVELOPMENT OF ANALYTICAL METHODS FOR MONITORING BURNUP

Two methods of determining the concentration of rare earth fission products in irradiated fast reactor fuels are under development. As discussed in the preceding subsection, the rare earths are considered ex-

cellent candidates as burnup monitors for oxide fuels because they are immobile in the fuel during irradiation. Current work on the two methods of analysis is discussed below.

1. Photometric Titration of Total Rare Earths (*R. J. Meyer, R. D. Oldham*)

Developmental work has continued on a method of determining total rare earths by a photometric titration with EDTA. A detailed outline of the procedure was given in a previous report (ANL-7425, p. 193). Separation of the rare earths from major interferences is achieved in two steps of the procedure: (1) anion exchange in concentrated hydrochloric acid to remove the bulk of the fuel and cladding constituents and some fission products and (2) anion exchange in a methanol-nitric acid solution to remove the alkali metals, the alkaline earths, and yttrium. Recent minor modifications in both of these steps have resulted in improved separations.

The anion-exchange separation with concentrated hydrochloric acid has been altered to provide a better separation of plutonium from the rare earths. This was accomplished by eluting the rare earths from the anion-exchange column with concentrated hydrochloric acid that is 1 *N* in nitric acid. In the absence of nitric acid, it had been found that the plutonium was not quantitatively absorbed by the resin and thus contaminated the rare earth eluant.

In the anion-exchange separation with methanol-

nitric acid, refinements were made to provide a better and more reproducible separation of the rare earths from yttrium; these were (1) closer control of the amount and height of resin in the column, (2) closer control of the methanol and nitric acid concentrations when the column is converted to this medium from a dilute nitric acid medium, and (3) reslurrying of the resin after this conversion to insure homogeneity of the column packing.

The modified procedure was tested using two mixtures of rare earths and yttrium. One mixture simulated that which would be produced by uranium-235 fission; the other mixture simulated that which would be produced by plutonium-239 fission. Three rare earth determinations were carried out on each mixture. Recoveries for the ^{235}U mixture were 100.5, 100.5, and 101.0% and for the ^{239}Pu mixture, 99.9, 100.4, and 100.6%.

Because the constituents of stainless steel interfered slightly in previous procedures, the effect of stainless steel was retested using the revised procedure. No interference was observed.

The procedure was evaluated by analyzing two

samples of irradiated UO_2 . One sample was declad prior to the dissolution; the other was not. The rare earth (R.E.) content and the cerium-144 gamma-count rate of each solution were determined. A comparison of the results obtained on the two solutions was made by means of the ratio $(\mu\text{mol R.E.}/\text{ml})/({}^{144}\text{Ce cpm}/\text{ml})$. Ratios of 1.597×10^{-5} and 1.613×10^{-5} were obtained for the declad and clad samples, respectively.

The determined rare earth content of each sample

differed by 6% from the value calculated from pre- and post-irradiation mass-spectrometric uranium analysis and the best available data for rare earth fission yields. Uncertainties in both the mass-spectrometric burnup analysis and the fission yield data could easily account for this difference. The agreement in the analyses of the clad and declad samples is a further substantiation that stainless steel constituents no longer interfere in the analysis.

No further work on this method is planned.

2. X-Ray Spectrometric Determinations of Rare Earth Fission Products (R. V. Schablaske, M. I. Homa)

Measurement of burnup in fast reactor fuels by an X-ray spectrometric assay of the rare earths is under development. The general analytical procedure to be used was described in ANL-7425, p. 194, and preliminary evaluations of the sensitivity and selectivity of the method were reported. In the proposed procedure, terbium (a rare earth not produced in fission) is added to the sample as an internal standard; the rare earth fraction is separated from uranium, plutonium, and high-activity fission products; and the separated rare earths are mounted on a metal plate and assayed by X-ray spectrometry.

Mounting the rare earth fission products as a solid on a metal plate provides the necessary sensitivity; however, a high degree of geometric reproducibility of the sample mount is difficult to achieve. This variability can be overcome by the introduction of an internal standard. The increase in precision achieved by this technique is demonstrated by the following experiment.

Six aluminum plates, each containing a total of 58 μg of inactive fission product rare earths and 8 μg of terbium internal standard, were prepared and assayed by measuring the La $L\alpha_1$, Ce $L\alpha_1$, Pr $L\alpha_1$, Nd $L\alpha_1$, and Tb $L\beta_1$ line intensities. Line-intensity ratios (rare earth/internal standard) were then calculated from the line-intensity data.

A comparison of the precision obtainable from absolute intensity data with the precision obtainable by use of an internal standard is shown in Table VII-2. For simplicity only the neodymium and terbium data are presented. The precisions of the line-intensity ratios for the other rare earths were similar to that shown for neodymium in Table VII-2. Relative standard deviations of the ratios for the $L\alpha_1$ lines were as follows: lanthanum, 4.3%; cerium, 2.9%; praseodymium, 2.8%; neodymium, 2.3%. The poorer precision for lanthanum is the result of a line intensity that

is significantly lower than that of the other rare earths.

In further testing of the internal-standard technique, a calibration curve was prepared using a series

TABLE VII-2. COMPARISON OF ABSOLUTE AND RELATIVE LINE INTENSITY DATA IN X-RAY SPECTROMETRIC RARE EARTH ANALYSIS; Nd = $L\alpha_1$, Tb = $L\beta_1$

	Nd (counts/sec)	Tb (counts/sec)	Nd/Tb
	159.9	61.5	2.60
	172.6	69.7	2.48
	176.8	66.8	2.65
	164.2	65.1	2.52
	125.7	48.9	2.57
	149.9	58.2	2.58
Average	158.2	61.7	2.57
Rel. Std. Dev.	11%	8%	2.3%

TABLE VII-3. RELIABILITY OF THE X-RAY SPECTROMETRIC ANALYSIS FOR COMBINED RARE EARTHS

Amount Present (μg)	Amount Found (μg)	Difference (%)
14.6	14.4	-1.5
	14.7	+0.7
29.2	28.8	-1.3
	29.6	+2.5
43.9	43.4	-1.2
	44.6	+1.6
58.4	58.8	-0.5
	59.2	+1.3
72.9	72.0	-1.3
	73.5	+0.8
87.9	86.6	-1.1
	88.5	+1.0

of 12 plates. Each plate contained 8 μg of terbium and a total of 15 to 90 μg of the principal fission product rare earths: lanthanum, cerium, praseodymium and neodymium. (The amounts of individual rare earths were based on their respective fission yields.) The La $L\alpha_1$, Ce $L\alpha_1$, Pr $L\alpha_1$, Nd $L\beta_1$, and Tb $L\beta_1$ line intensities were measured, and line-intensity ratios (rare earth to internal standard) were calculated from the line-intensity data. Calibration curves (line ratio *vs.* composition) were then derived from a least-squares analysis of the data.

To evaluate the calibration curves prepared from this data, the actual concentration of each rare earth on each plate was compared with that calculated using the measured line intensity and the calibration curve. When the total weight of the rare earth mixture was 30 to 90 μg , the average relative error calculated for each rare earth was as follows: lanthanum, 1.9%; cerium, 1.6%; praseodymium, 1.1%; and neodymium, 1.1%. When the total weight of the mixture was <30 μg , the errors were somewhat larger due to low line intensities.

Typical results were as follows:

Rare Earth	Amount (μg)	
	Present	Found
Lanthanum	11.6	11.8
Cerium	21.5	21.9
Praseodymium	9.7	9.8
Neodymium	37.8	37.9

A further evaluation of the data obtained in the calibration study showed that summing the four individual rare earths provides a more sensitive method of analysis with no decrease in precision. The data shown in Table VII-3 demonstrate that in the range

from 15 to 90 μg of combined rare earths, a precision of 1 to 2% is obtained. It is anticipated that the lower limit could be extended to 5 μg by increasing the counting time in the X-ray spectrometer from 1 to 3 hr.

Attention is now being given to the development of a simple separation procedure which will isolate the rare earths in a form suitable for X-ray spectrometry. A successful separation must meet at least two criteria: (1) the separated rare earths must be free of other elements that emit X-rays in the region of the L-spectra of the rare earths, and (2) the separated rare earths must be free of such bulk constituents as uranium, plutonium, and cladding. The latter criterion is necessary because the L-spectra of the rare earths consist of very soft X-rays which are easily absorbed by other solids.

Anion exchange in hydrochloric acid is being considered as a means of separating the rare earths from the bulk constituents of the fuel and cladding. This separation, which is one step in the rare earth photometric titration described above, is expected to be well suited to the X-ray spectrometric analysis, provided that the reagents do not introduce solids onto the X-ray plates.

In preliminary tests of the anion-exchange procedure, only the terbium internal standard and a simulated mixture of fission product rare earths were used. X-ray analysis of the "separated" rare earths showed no change in the individual rare earth-to-terbium ratios. However, the intensities of the "separated" rare earths were significantly lower than those of directly plated standards.

It is believed that this decrease in intensities resulted from small amounts of solids on the "separated" rare earth plates. Investigation of the source of the solids will be necessary before proceeding with testing of the anion-exchange separation.