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**Characterization of Insoluble
Residues From the Dissolution
of Irradiated (U,Pu)O₂**

J. H. Goode
P. C. Arwood

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CONSOLIDATED FUEL-REPROCESSING PROGRAM

✓ CHARACTERIZATION OF INSOLUBLE RESIDUES FROM THE DISSOLUTION OF IRRADIATED (U,Pu)O₂

J. H. Goode
P. C. Arwood

Chemical Technology Division

Date Published: May 1983

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CHARACTERIZATION OF INSOLUBLE RESIDUES FROM THE DISSOLUTION OF
IRRADIATED (U,Pu)O₂

J. H. Goode
P. C. Arwood

ABSTRACT

Hot-cell tests were conducted using (U,Pu)O₂ fuels that had been irradiated to about 5.2 TJ/kg (U + Pu) [60 MWd/kg (U + Pu)] in an effort to characterize the insoluble residues that remained after the fuel pellets had been dissolved in HNO₃ and in HNO₃-KF. The composition, particle size range, and density of the material were determined by newer analytical techniques, including spark-source mass spectrometry, neutron activation, scanning electron microscopy, and X-ray fluorescence, combined with older methods such as sedimentation and powder density by water displacement.

1. INTRODUCTION

When highly irradiated reactor fuels such as UO₂ or (U,Pu)O₂ are dissolved in nitric acid for the recovery of uranium and plutonium, an intensely radioactive, insoluble residue remains (Fig. 1). This residue should be removed before solvent extraction to prevent emulsification or possible formation of deposits in the processing equipment. Analyses of this separated material by techniques such as emission spectroscopy, radiochemistry, and scanning electron microscopy have generally identified undissolved, plutonium-rich (U,Pu)O₂ and the nitric acid-insoluble fission products.¹⁻³

Many of the fission products migrate to the grain boundaries of the fuel during irradiation. The composition of these fission product inclusions is thought to be dependent on the radial oxygen-to-metal (O/M) ratio of the fuel. The particle size is dependent on the burnup or length

ORNL-PHOTO 1229-81

Fig. 1. Insoluble residue from the dissolution of irradiated $(U,Pu)O_2$.

of the irradiation period, the temperature, and both the axial and radial temperature gradients. The size of the fission product particles can vary from newly born submicron particles within the fuel grain to the large noble metal "ingots" that have reportedly been found at the bottom of the central hole in restructured fuel rods.

The uranium and plutonium contents of the residues have been shown to be dependent on the fabrication and irradiation history of the reactor fuel. Homogeneous, solid-solution $(U,Pu)O_2$, containing less than 35% PuO_2 , is almost completely soluble in nitric acid.³ Nonhomogeneous, plutonium-rich oxides require a catalyst such as fluoride for complete dissolution. The major fission product elements usually include molybdenum, technetium, ruthenium, rhodium, and palladium (plus others) in varying proportions.

For some time hot-cell work, sponsored by the Consolidated Fuel Recycle Program, has emphasized the determination of some of the physical characteristics of residues that would be needed for the design of feed clarification equipment. In particular, we are interested in the composition of the residue particles, as well as the density and the particle size distribution of the material.

Most of this experimental work was performed using the remnants from the postirradiation, destructive examination of full-length Fast Flux Test Reactor (FFTF) $(U,Pu)O_2$ fuel rods from the PNL-59 series which had been irradiated in the General Electric Test Reactor (GETR).⁴ These fuel-rod segments were furnished to ORNL by the Hanford Engineering Development Laboratory (HEDL). Other residue density tests were conducted^{5,6} with fuel-rod remnants from the PNL-3 and P-15 irradiation experiments in the GETR and in the Experimental Breeder Reactor No. 2 (EBR-2), also obtained from HEDL.⁷ The fuel pellets were fabricated by HEDL or by FFTF commercial vendors and were assembled into fuel rods by HEDL. The PuO_2 contents of the mixed oxide pellets prior to irradiation varied from 22.8 to 27.3%; the balance was UO_2 of natural enrichment.

2. EXPERIMENTAL

The insoluble residues were prepared by dissolving up to ~1 kg of 1-in. (2.5-cm) segments of fuel rods in 7 M HNO_3 for about 4 h at 95°C to a final concentration of about 200 g (U + Pu)/L. The residue (DS-1R) was centrifuged from the dissolver solution (DS-1), washed with 3 M HNO_3 , and leached a second time with 3 M HNO_3 for 4 h at 95°C (DS-2). Any undissolved uranium or plutonium in the twice-leached residue (DS-2R) was then determined by refluxing the residue in 8 M HNO_3 -0.05 M KF for 2 h (DS-3). This procedure is known to dissolve essentially all of the (U,Pu) O_2 , leaving a fission product residue (DS-3R).

The residues were analyzed as follows:

1. composition — a combination of spark-source mass spectrometry (SSMS), neutron activation analysis (NAA), and radiochemical analysis (RCA) techniques;
2. particle size — the distribution was determined by sedimentation and Stokes' law calculations;
3. density — measured directly by the displacement of water from a small pycnometer.

3. RESULTS AND DISCUSSION

3.1 COMPOSITION OF THE RESIDUE

3.1.1 Uranium and Plutonium Contents

In the first experiment of this series, the uranium and plutonium in the insoluble residue were determined by standard high-temperature fusion of an aliquot of residue into sodium carbonate. The fused salt was dissolved in HCl and filtered; the resulting solution was then subjected to fluorometric uranium and radiochemical plutonium analyses. Any undissolved residue was fused again. This time-consuming procedure indicated that complete dissolution of a 10-mg aliquot of residue could require two or three successive fusions in sodium carbonate in platinum crucibles. The large dilution factors resulting from multiple fusions led to low plutonium alpha counting rates and, in turn, considerable error in the analysis. A stronger fusion reagent, such as potassium pyrosulfate, would dissolve

the PuO_2 more rapidly; however, it would also volatilize the ruthenium and cause large errors in that determination. (Such errors were suggested by results from other, earlier studies which had poor ruthenium material balances.) As an example, a 10-mg aliquot of residue in experiment FBR-30 was fused twice in Na_2CO_3 and then once more in $\text{K}_2\text{S}_2\text{O}_7$ to clean the "empty" crucible. The plutonium recoveries were as follows:

Na_2CO_3 fusion 1	- 0.36 mg Pu
Na_2CO_3 fusion 2	- 0.03 mg Pu
$\text{K}_2\text{S}_2\text{O}_7$ fusion 3	- <u>0.10 mg Pu</u>
Total	0.49 mg Pu

This result indicated the need for faster, more reliable methods of analysis for both the plutonium and the gamma-emitting fission products. The uranium content was typically 9.1 mg per gram of residue.

In the interest of improving the speed and the accuracy of analysis of the residues, a combination of nondestructive NAA and gamma spectroscopy was used to determine the plutonium and the gamma-emitting fission products in weighed aliquots of the residue. This technique was possible because normal-enrichment uranium was used in the fabrication of the $(\text{U},\text{Pu})\text{O}_2$ in these pellets, rather than the enriched uranium used in so many earlier experimental fuel rods.

Milligram-scale, weighed aliquots of residue were removed from the hot cell, encapsulated in polyethylene vials, and irradiated along with plutonium standards in the pneumatic irradiation facility of the Oak Ridge Research Reactor (ORR). Following irradiation, the plutonium content of each aliquot was determined by delayed neutron counting; gamma spectroscopy was used to measure the fission product content on a per gram-of-residue basis. Material balances for plutonium and ^{106}Ru -Rh were improved over those determined by using the fusion methods.

Good agreement was obtained between the plutonium content of the residue after nitric acid leaching and the sum of the plutonium in the HNO_3 -KF leach solution and the fluoride-leached residue. For example, in experiment FBR-30, NAA results indicated that the HNO_3 -leached residue

contained about 0.49 mg of plutonium. The fluoride leach solution and the leached residue contained 0.29 and 0.11 mg of plutonium, respectively, giving an 82% material balance. (The uranium contents of the residues, however, could not be determined by NAA in the presence of the plutonium; prior experience had shown that essentially all of the uranium is dissolved from the residues by the nitric-fluoride leach.)

Similar good results were obtained when the NAA technique was used to determine the plutonium in leached cladding. In experiment FBR-31, neutron activation of a 1-cm segment of leached stainless steel cladding showed the presence of 50.1 μg of plutonium. Extensive chemical dissolution of a companion piece of the cladding, followed by RCA analysis, indicated the presence of 51.2 μg of plutonium. This agreement was adequate for our purposes.

3.1.2 Fission Product Contents of Residues

Gamma spectroscopy indicated that $^{106}\text{Ru-Rh}$ and ^{125}Sb were the principal gamma-active nuclides in leached residues. Smaller quantities of ^{137}Cs , ^{110}Ag , ^{60}Co , and other nuclides were sometimes present. Few data on beta-emitters and other fission products were available.

A shielded, in-cell, spark-source mass spectrometer for highly gamma- and alpha-active samples was used for the direct analyses of both liquid and solid samples of dissolver solutions and insoluble residues.⁸ Individual electrodes were prepared by pipetting an aliquot of solution or by adding solids to the cavity on the tip of the graphite electrode using master-slave manipulators. The electrodes were then inserted with manipulators into the heavily shielded instrument and repeatedly "sparked" to ionize the components of the samples. (In a later development, internal erbium standards were added to the samples.) A typical spectrum of a dissolver solution is shown in Fig. 2. A typical residue analysis, before and after the $\text{HNO}_3\text{-KF}$ leach, is shown in Table 1.

All of the SSMS results for one of the first highly active tests, FBR-35, are shown in Table 2. In the last two columns, the amount

A. TRIPLY-CHARGED U, Pu	D. HEAVY FISSION PRODUCTS
B. LIGHT FISSION PRODUCTS	E. ERBIUM STANDARD
C. DOUBLY CHARGED U, Pu	

Fig. 2. Mass spectrum of FBR dissolver solution.

Table 1. Composition of insoluble residue (Run FBR-35)

Nuclide	Fraction of residue (wt %)	
	Before HNO ₃ -KF leaching	After HNO ₃ -KF leaching
U	11.7	0.1
Pu	23.1	<0.1
W ^a	0.7	4.5
Ag	2.3	1.4
Pd	4.0	8.3
Rh	15.3	18.8
Ru	27.1	37.3
Mo	11.7	22.7
Tc	3.9	6.9
Fe, etc.	0.1	-

^aFrom ball mill in pellet preparation.

actually found by analysis and that calculated using ORIGEN are compared on the basis of $\mu\text{g/g}$ (U + Pu).^{9,10} Many of the values are remarkably close; however, further refinements of the method involving correction of elemental sensitivity factors and use of internal standards are recognized as necessary future improvements to the accuracy of the analysis.

Note especially the similarity in the noble metals in the residue before (DS-2R) and after (DS-3R) HNO₃--KF leaching, and how the uranium and plutonium had dissolved in the leachant (DS-3). Also note the comparisons for total uranium and plutonium that had been analyzed by different (SSMS, NAA, radiometric, or other) methods.

The SSMS technique proved to be sensitive enough to permit determination of many of the individual abundances. It was noted that many varied from those predicted by ORIGEN calculations. For example, Warmack,⁸ formerly of the ORNL Analytical Chemistry Division, determined that the abundances for molybdenum and palladium in the dissolver solution (DS-1)

Table 2. Distribution of fuel and fission products during dissolution (run FBR-35)

Element	Sample (and volume or weight) ^a						(μg/g (U + Pu))	
	DS-1	DS-2	DS-2R	DS-3	DS-3R	Total	Fuel	ORIGEN
	(80 mL)	(103 mL)	(0.1336 g)	(112 mL)	(0.0922 g)	(μg)		
U	1.17 x 10 ⁷	30,900	~15,982 ^c	5488 ^c 4300 ^d	58 ^c	1.18 x 10 ⁷ = 11.8 g ^c 11.7 g ^d		
Pu	3.96 x 10 ⁶	41,200	26,500 ^e ~31,400 ^c	10,400 (α) ^b	5 ^e	4.04 x 10 ⁶ = 4.04 g ^c 4.04 g(α) ^b		
W	4,000		956		4,149	8,149		
Ag	6,800	100	3,142	56	1,290	10,042	636	272
Pd	168,000	618	5,464	336	7,560	176,514	11,172	3,090
Rh	8,000	1,030	20,763	560	17,149	29,793	1,886	1,233
Ru	15,200	1,854	36,882	1,120	34,114	53,936	3,414	3,396
Mo	40,000	1,545	15,982	448	20,745	62,738	3,971	4,089
Tc	6,800	381	5,327	112	6,270	13,563	858	1,073
Fe	32,000	7,725	164	1,120	83	40,928		
Cr	16,000	1,545		224		17,769		
Ni	16,000	1,339				17,339		
Nd	24,000	206			4	240,210	15,203	4,406
Ba	136,000	72				136,072	8,612	1,751
La	48,000	31				48,031	3,040	1,427
Cs	640,000	31	5	45	8	640,084	40,512	3,602
Te	288,000	185	6			288,191	18,240	793
Eu	12,800					12,800	810	158
Ce	88,000	62	1			88,063	5,574	2,767
Pr	48,000	31				48,031	3,040	1,372
Sm	24,000					24,000	1,519	1,236
Zr	88,000	18	8		20	88,046	5,573	3,268
Sr	20,000	18				20,018	1,267	521

^aUnits in table are μg.^bBy alpha analysis.^cSSMS analysis.^dColorimetric, titrimetric, or fluorometric analysis.^eNAA analysis.

of run FBR-35 were high in ^{95}Mo , while those for the leached residue abundances were low, and vice versa for ^{106}Pd (Table 3). This appears to indicate that moderately long-lived precursors affect the fate of their daughters (i.e., mass 95 behaved more like zirconium than molybdenum, and mass 106 more like ruthenium than palladium. Sites,¹¹ also of the ORNL Analytical Chemistry Division, reported that the silver in the dissolution residues was predominantly ^{109}Ag . A more-detailed analysis of this type of data would be valuable.

Table 3. Isotopic abundances of molybdenum and palladium

	ORIGEN abundance	Run FBR-35		
		DS-1	DS-2R	DS-3R
^{95}Mo	0.211	0.60	0.052	0.064
^{97}Mo	0.237	0.13	0.28	0.27
^{98}Mo	0.252	0.13	0.28	0.29
^{100}Mo	0.298	0.14	0.38	0.38
^{105}Pd	0.313	0.48	0.21	0.24
^{106}Pd	0.288	0.10	0.65	0.55
^{107}Pd	0.202	0.23	0.087	0.11
^{108}Pd	0.141	0.15	0.044	0.076
^{110}Pd	0.040	0.032	0.0077	0.019

3.1.3 Fraction of Elements Insoluble in Residues

The fractionation of many of the fission product elements was noted when the insoluble residues were analyzed by SSMS (Table 4). It may be observed, for example, that large fractions of the rhodium and ruthenium (up to greater than 90% in some tests) and about one-half of the technetium or molybdenum failed to dissolve. These results would affect calculations of the fission product concentrations in solvent extraction feed, the composition of high-level wastes, etc.

Table 4. Solubility of fission products in nitric acid
(Run FBR-35)

Fission product	HNO ₃ -insoluble fraction (% of total)
Ag	31
Pd	4
Rh	70
Ru	68
Mo	33
Tc	46

The amount of ruthenium in replicate samples (A or B) of residue from high burnup segments of fuel rods, before (DS-2R) and after (DS-3R) leaching with HNO₃-KF, was found to be essentially constant (Table 5).

Table 5. Ruthenium contents of residues

Run No.	Residue No.	Ruthenium content, ^a 10 ⁶ Ru (GBq/g residue)
30	DS-2R	120
30	DS-3R	120
31	DS-2(A)	163
31	DS-2(B)	100
31	DS-3(A)	110
31	DS-3(B)	113
32	DS-2R(A)	164
32	DS-2R(B)	96
32	DS-3R(A)	178
32	DS-3R(B)	128
33	DS-2R(A)	160
33	DS-2R(B)	161
	Average	134 ± 29

^aBased on common decay date (12/1/80).

3.1.4 X-ray Fluorescence and Scanning Electron Microscope Examination

Scanning electron microscope (SEM) samples were prepared in the hot cell, coated with carbon, and subjected to SEM examination and X-ray fluorescence (XRF) analysis. Figure 3 shows dried residue particles which had molybdenum, ruthenium, and technetium as the major components. Based on SSMS results, rhodium and palladium are probably present but are off scale (>20 keV) or were not resolved by the x-ray spectra. Figure 4 shows an irregular particle of stainless steel corrosion product contaminated with molybdenum and ruthenium. Figure 5 shows a "trash" particle containing a number of light elements. Figure 6 is a 3- μ m-diam residue particle containing molybdenum, ruthenium, and technetium and contaminated with tungsten from a ball mill used in the fuel pellet preparation. The last spectrum (Fig. 7) is of a fuel particle (lower right of photograph) that shows peaks for uranium, plutonium, ruthenium, molybdenum, and tungsten.

3.2 DENSITY OF DISSOLUTION RESIDUES

The density and size distribution of the particles comprising a dissolver residue should be known in order to adequately design a centrifugal device for removing dissolver residues from solution. The density of the dried residue [resulting from two leaches of (U,Pu) O_2 with nitric acid] was determined directly by the displacement of water from a 0.5-mL Pyrex pycnometer (Fig. 8). Weighings were performed on a 160-g-capacity Torbal analytical balance in the hot cell using master-slave manipulators. About 1.08 g of twice-leached residue from the dissolution of ~ 1 kg of irradiated (U,Pu) O_2 was obtained from the Solvent Extraction Test Facility (SETF)⁷ for the experiments by backwashing a 1- μ m-porosity etched-disc filter with 3 M HNO_3 and permitting the slurry to resettle.

The following standard technique was used:

1. Weigh the clean, dry, empty pycnometer.
2. Weigh pycnometer filled with freshly boiled distilled water; note temperature. Empty and dry the pycnometer.
3. Weigh dry solids in the dry pycnometer.

Fig. 3. SRF spectrum of dried dissolver residue particles (PNL-59-65).

Fig. 4. XRF spectrum of light particle in dissolver residue (PNL-59-66).

Fig. 5. XRF spectrum of trash particle in dissolver residue (PNL-59-66).

Fig. 6. XRF spectrum of dissolver residue particle (PNL-59-66).

Fig. 7. XRF spectrum of (U,Pu) particle in dissolver residue (PNL-59-66).

Fig. 8. Pycnometer for density determination.

4. Fill pycnometer with freshly boiled distilled water; mix to wet the solids; weigh; note temperature.
5. Calculate weight/volume of water displaced by the solids.
6. Calculate weight of solids/volume of solids (Appendix A).
7. Repeat three or four times.

Using this method, four separate determinations of the density of an FFTF UO₂ blanket pellet were made as a means of standardizing the equipment prior to analyzing the powdered fission product residue. Results of these tests indicated that the average density of the UO₂ pellet was 10.46 g/cm³.

The average density of two batches of fission product solids remaining after two nitric acid leaches was 7.74 g/cm³. When the solids were leached additionally with more 8 M HNO₃-0.05 M KF to dissolve residual (U,Pu)O₂, the apparent density was slightly increased to 8.32 g/cm³. This increase may signify the dissolution of light element "trash" (including silicates) or part of the fission product oxides; also, it may indicate that (U,Pu)O₂ leaves a heavier, more "metallic" residue. Results of SSMS analyses of the residue before and after leaching with HNO₃-KF indicated that the fluoride leach solution (DS-3) contained significant amounts of iron as well as ruthenium, rhodium, and molybdenum.

The relatively low densities of the residues (7 to 9 g/cm³) may result from the presence of low-density impurities (suggested by the increase in density after the fluoride leach) or from part of the undissolved fission products being present as oxides (~7 g/cm³) or carbides rather than as metals (10 to 12 g/cm³). Mass spectrometry data do not preclude the possibility of the presence of carbides of molybdenum, technetium, ruthenium, etc., in the residue (because these compounds have the same mass and could be interpreted as impurities such as cadmium, indium, and tin). The carbides could also be artifacts from the graphite electrode used in SSMS.

3.3 DETERMINATION OF THE PARTICLE SIZES OF THE RESIDUES

The insoluble residues at different stages of leaching were concentrated from the dissolver solutions by extended (30 to 45 min)

centrifugation at about 2200 rpm in a clinical centrifuge. The residues were washed thoroughly with 3 M HNO₃ (or some other reagent) and dispersed in about 2 mL of the reagent via 10 to 30 min of agitation in an ultrasonic bath. (Residues for sedimentation tests were never allowed to dry, but were kept under acid.) The particle size range was determined by sedimentation of the concentrated residue in a graduated glass column containing a mixture of 40% glycerine in distilled water. After timing the fall of the largest (and heaviest) particle agglomerates to the bottom of the column of glycerine, a series of successive, timed samples was rapidly removed (Fig. 9), starting from the top of the liquid column, until the entire volume had been divided into equal-volume samples of residue in the glycerine. Each of these samples was centrifuged to concentrate the material into the bottom of the centrifuge cone. The gamma activity of the residue in each tube was then determined using a fixed geometry with an in-cell radiation meter. In some cases, the residues were washed, dried, and then weighed. The weight of residue in each cone was found to be approximately proportional to its gamma activity (above).

Stokes' law was subsequently used to calculate the particle size distribution (equivalent hydrodynamic diameter) of the residue since the time and distance settled, the temperature, and the viscosity and density of the residue and medium were all known (Appendix B):

$$V = \frac{gd^2(\delta - \rho)}{18\eta} \quad (\text{Stokes' Law}) \quad (1)$$

where

- V = terminal velocity, cm/s,
- g = standard gravity, cm/s²,
- d = hydrodynamic diameter of equivalent sphere, cm,
- δ = particle density, g/cm³,
- ρ = fluid density, g/cm³,
- η = fluid viscosity, Poise (= 0.1 Pa.s).

$$V = h/t, \quad (2)$$

where

DETERMINATION OF PARTICLE SIZE DISTRIBUTION

FBR-37-12; SOLIDS CONCENTRATED IN DISSOLVER
SOLUTION; SETTLED IN 40% GLYCEROL; 31.5°C

Fig. 9. Determination of particle size distribution.

h = height of fall, cm,

t = time of fall, s.

Rearranging,

$$d = \left(\frac{18\eta(h/t)}{g(\delta - \rho)} \right)^{1/2} \quad (3)$$

A typical calculation for the largest particles in run FBR-36 (i.e., the first particles to settle to the bottom of the tube) would be:

$$\begin{aligned} d &= \left(\frac{18 \times 0.0144 (22 \text{ cm}/25 \text{ s})}{980.665 \times (7 - 1)} \right)^{1/2} \\ &= 0.00623 \text{ cm} \\ &= 62.3 \text{ } \mu\text{m}. \end{aligned}$$

Calculations for a typical run are shown in Appendixes B and C; plots from five tests showing the measured size distribution of the residues are presented in Fig. 10. Figure 10 indicates that greater than 99% of the particles are larger than 1.5 μm in diameter and more than 30% are larger than 15 μm . The largest particles ranged from 60 to 125 μm in diameter.

The acidity of the medium apparently plays a role in the agglomeration of the individual particles into larger units. A residue dispersed in water is often peptized and colloidal in nature, while a 4 M HNO_3 dissolver solution contains much larger particles (Figs. 11 and 12). Aggregation of the small particles, which is clearly indicated, is affected by solution composition (acidity). It could also possibly be affected by the glycerine or other constituents or by the increased concentration of solids (i.e., grams of residue per milliliter of solution) as a result of centrifugation. These are not the same as in actual dissolver solutions. Further tests are needed to confirm that the particle sizes measured here are the same as those in actual process solutions.

Fig. 10. Size distribution of dissolution residues.

Fig. 12. Size distribution of residue in 4 M HNO₃ dissolver solution.

Fig. 11. Size distribution of residue as a function of nitric acid acidity.

4. ACKNOWLEDGMENTS

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6. APPENDIXES

6.1 Appendix A: Density of Solids by Displacement of Water

The weights and calculations pertinent to determining the density of a UO₂ pellet are tabulated below (all values are in grams):

a. Pycnometer filled with water	9.0184
b. Clean, dry pycnometer	<u>8.4362</u>
c. Weight of water in full pycnometer	0.5822
d. Pycnometer + pellet	9.7266
e. Empty pycnometer	<u>8.4362</u>
f. UO ₂ pellet	1.2904
g. Pycnometer + pellet + water	10.1867
h. Pycnometer + pellet	<u>9.7266</u>
i. Weight of water in pycnometer	0.4601
(0.4604, 0.4600 g in two other determinations; Av. = 0.4602)	
j. Weight of water when full	0.5822
k. Weight of water with pellet	<u>0.4602</u>
l. Weight of water displaced	0.1220 = volume of pellet
m. Weight of pellet	<u>1.2904g</u>
n. Volume of pellet	0.1220 cm ³ = $\frac{1.2904 \text{ g}}{10.5770 \text{ g/cm}^3}$ density of pellet

Similarly, the weights used in the calculations of the powdered residue were:

Pycnometer + dry residue	9.0899
Dry, clean pycnometer	<u>8.4338</u>
Dry residue	0.6561
Pycnometer + solids + residue	9.5901
Pycnometer + residue	<u>9.0899</u>
Water left in pycnometer	0.5002
(0.5002, 0.4974, 0.4955, 0.4926, 0.5058)	

Weight of water in full pycnometer	0.5822
Weight of water left	<u>0.4984</u>
Weight of water displaced	0.0838 = volume of powder
Weight of residue	<u>0.6561</u> g
Volume of residue	$\frac{0.6561 \text{ g}}{0.0838 \text{ cm}^3} = 7.8294 \text{ g/cm}^3,$ density of residue

6.2 Appendix B: Viscosity and Density of LMFBR Dissolver Solutions

The viscosities of several highly irradiated LMFBR dissolver solutions were determined by comparison with the viscosities of five known solutions. We prepared solutions of distilled water, and of 20, 40, 50, and 60 wt % CP glycerine-in-water, and measured the time of their discharge through the capillary tip of a 25-mL buret at a series of temperatures. A calibration chart was then constructed using the handbook values for the viscosities of the solutions (Fig. B.1). The chart shows three curves: one for the discharge of 25.0 mL, one for the complete emptying of the buret (~30 mL) at the usual June ambient cell temperature (31.5°C), and a third showing the time to empty the buret at 23.5°C. The accuracy of the calibration chart was verified by measuring the viscosities of known $\text{Ca}(\text{NO}_3)_2$ -in-water (+5%) and sucrose-in-water (+2%) solutions.

Densities (specific gravities) of the centrifuged LMFBR dissolver solutions were determined by replicate, repetitive weighings of 10.0-mL volumes of the solutions on a calibrated analytical balance. The same solutions were analyzed for uranium, plutonium, and free nitric acid. The viscosity of each solution, in centipoises (cP), could then be calculated from its kinematic viscosity, in centistokes (cSt), and specific gravity:

$$\text{cP} = (\text{cSt})(\text{sp gr}).$$

The results of the replicate tests, summarized in Table B.1, indicate that the viscosity of a 200 g (U + Pu)/L-4 M HNO_3 solution is ~1.6 to 1.8 cP. This value is slightly less (i.e., the solution is more fluid) than the 40% glycerol-in-water (~2.7 cP) used for the residue sedimentation tests. Figures B.2 and B.3 illustrate the test results.

Table B.1. Summary of density-viscosity tests on LMFBF
dissolver solutions

Run No.	Acidity (M)	Concentration (U + Pu) (g/L)	Density ρ (g/cm ³)	Delivery time(s)		Viscosity ^b	
				Open ^a	25 mL	cSt	cP
30	4.33	199	1.44	42.9	32.9	1.15/1.15	1.66
31	4.28	118	1.31	42.7	32.6	1.10/1.03	1.39
32	5.96	232	1.50	42.7	32.7	1.10/1.07	1.64
33	5.23	174	1.42	42.8	32.7	1.10/1.08	1.55
34	4.68	171	1.41	43.2	32.8	1.22/1.12	1.65
35	4.47	195	1.44 (calc.)	NA	NA	NA	NA
36	4.46	201	1.43	43.4	33.2	1.27/1.25	1.80
37	4.10	166	1.43	42.9	32.9	1.13/1.12	1.61

^aOpen signifies time required to complete emptying of buret (~30 mL).

^bOne centipoise = 1.00 mPa.s; 1.00 centistoke = 10⁻⁶ m²(s⁻¹).

ORNL DWG 83-198

Fig. B.1. Calibration curve for viscosity in 25-mL buret.

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Fig. B.2. Densities of dissolver solutions of (U,Pu)O₂ in nitric acid.

ORNL DWG 83-218

Fig. B.3. Kinematic viscosities of dissolver solutions of (U,Pu)O₂ in HNO₃.

6.3 Appendix C: Residue Results from SETF

Table C.1. Data from SETF-2, Test 4^a

Sample No.	Sol. depth (cm)	Time (s)	Rate (mm/s)	ϕ (μm)	Net reading (mR/h)	% total smaller than	Cumulative Smaller than	% indicated Larger than
1	3.4	190 ^b	0.181	11.8	5100	25.0	25.0	75.0
2	6.8	229	0.297	15.1	4400	21.6	46.6	53.4
3	10.2	268	0.381	17.1	900	4.4	51.0	49.0
4	13.5	308	0.438	18.4	800	3.9	54.9	45.1
5	16.9	347	0.487	19.4	1300	6.4	61.3	38.7
6	20.3	386	0.526	20.1	1600	7.8	69.1	30.9
7	>20.3	>386	0.526	>20.1	6300	30.9	100.0	

^aProcedure: (1) remove 3 M HNO₃ from solids by centrifugation; (2) mix solids with 2 mL of 0.5 M HNO₃ and allow to equilibrate for 24 h; (3) disperse solids in 0.5 M HNO₃ in ultrasonic bath for 30 min; (4) float dispersed solids on 40% glycerol; (5) sample; (6) cell temperature, 29°C; $\eta = 0.0279$ P. See Fig. C.1.

^bSee Stokes' Law (Eq. 1) for largest particles: $[18 \times 0.0279 (22/151)/(980.665)(6.65)]^{1/2} = 33 \mu\text{m}$.

Fig. C.1. Size distribution of residue from SETF dissolution.

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