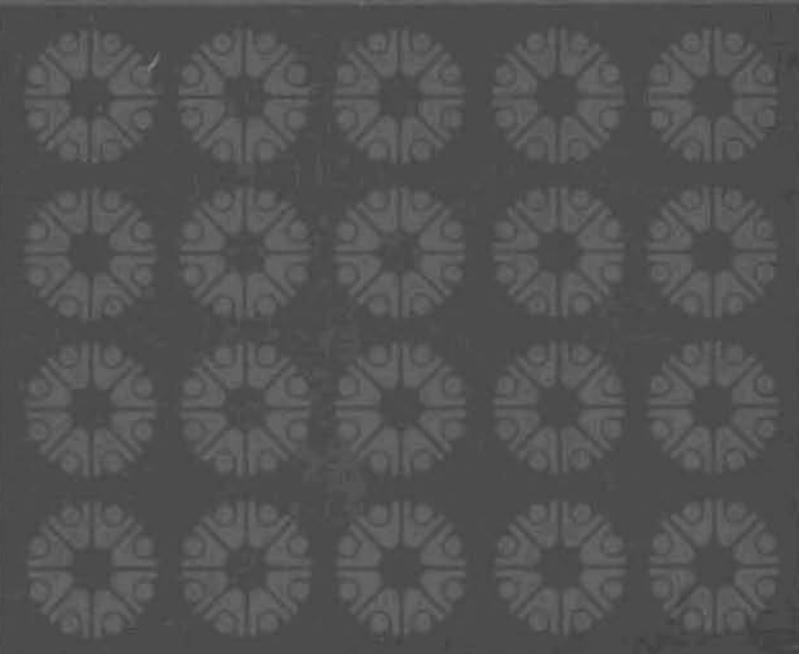




AEC Research and Development Report

DISSOLUTION PROPERTIES OF UO_2 - PuO_2 THERMAL REACTOR FUELS

June 1971



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BATTELLE
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U.S. ATOMIC ENERGY COMMISSION
Under Contract AT(45-1)-1830

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

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BNWL-1581

UC-80, Reactor
Technology

DISSOLUTION PROPERTIES OF UO_2 - PuO_2
THERMAL REACTOR FUELS

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June 1971

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ABSTRACT

Dissolution experiments were conducted to investigate the effects of fabrication variables and irradiation on the dissolution properties of UO_2 - PuO_2 thermal reactor fuels. Both irradiated and unirradiated cold-press-sinter pellet and vipac fuels were examined. Variables investigated include pressing pressure, sintering time and temperature, and burnup.

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DISSOLUTION PROPERTIES OF UO_2 - PuO_2
THERMAL REACTOR FUELS

1.0 INTRODUCTION

This report describes uranium-plutonium oxide fuel dissolution experiments conducted at the Pacific Northwest Laboratory as a part of the Plutonium Utilization Program. The successful utilization of uranium-plutonium mixed-oxide fuels in thermal reactors requires that suitable technology be available for reprocessing such fuels. For the foreseeable future, such reprocessing will be accomplished by the Purex process, an aqueous solvent extraction technique.

Fuel dissolution in nitric acid solution is an essential head-end step in the Purex process. Plutonium dioxide is, however, virtually insoluble in boiling concentrated nitric acid.^(1,2,3) Addition of fluoride to nitric acid greatly increases the dissolution rate of PuO_2 , but leads to increased vessel corrosion^(4,5) and complicates solidification of Purex process wastes for ultimate disposal.⁽⁶⁾

Uniform solid solution uranium-plutonium oxide fuels can be prepared by coprecipitation of uranium (VI) and plutonium (IV) ions from ammonical solutions followed by ignition and hydrogen reduction of the precipitate. Non-uniform solid solution $(U, Pu)O_2$ fuels are prepared by compacting mixtures of ceramic grade plutonium and uranium dioxide powders followed by high temperature sintering in a reducing atmosphere.^(7,8,9) It has also been suggested that some degree of solid solution formation occurs in mechanically-mixed UO_2 - PuO_2 fuel during irradiation.^(1,10) The formation of solid solutions has been shown to have dramatic effects on the dissolution properties of uranium-plutonium mixed oxide fuels.^(1,11,12)

Successful reprocessing of thermal reactor mixed oxide fuel by the Purex process thus requires a knowledge of how the dissolubility* and dissolution rate of such fuels are affected by their fabrication and irradiation histories. Such information is essential for equipment and flowsheet design and criticality control in the dissolver vessel. For these reasons this study has focused on the dissolution of mixed oxide thermal reactor fuels in 12 M nitric acid solutions.

2.0 SUMMARY

Several aspects of the dissolution behavior of UO_2 - PuO_2 thermal reactor fuels were investigated. The dissolubility of unirradiated cold-press-sinter pellet fuel containing UO_2 - 4 wt % PuO_2 was examined as a function of fuel pellet pressing pressure and sintering conditions. It was found that with a pressing pressure of 32,000 PSI and a sintering time of 6-10 hours at 1650° - 1700° C, sufficient UO_2 - PuO_2 solid solution formation occurs to render the fuel readily soluble in boiling 12 M nitric acid. No direct correlation between pellet pressing pressure and dissolubility was observed for pressures in the range 32,000 - 56,000 PSI. Cold-press-sinter pellet fuel rods which had been irradiated to a maximum burnup of 11,700 MWD/MTM were likewise found to be readily soluble in boiling 12 M nitric acid.

Dissolution rate studies with unirradiated UO_2 - 4 wt % PuO_2 cold-press-sinter pellet fuel indicated that little or no preferential dissolution of UO_2 takes place in boiling 12 M nitric acid when the fuel has been sintered 8-10 hours at 1650° - 1700° C. Thus, large accumulations of undissolved PuO_2 during dissolution of such fuels should be considered unlikely when the terminal nitric acid concentration remains near 12 M.

*Dissolubility as used here refers to the fraction of plutonium and uranium which dissolves when the mixed oxide fuel is exposed to boiling nitric acid for a short time [<24 hours].

However, with unirradiated, pneumatically impacted, vibrationally compacted (vipac), mixed-oxide fuel material containing 2-4 wt % PuO_2 , the situation was different. Between 60 and 70% of the PuO_2 present remained undissolved after a 6-hour exposure to boiling 12 M nitric acid. This is not unexpected since this type of fuel material is prepared from a mechanical mixture of UO_2 and PuO_2 powders without the sintering treatment necessary for UO_2 - PuO_2 solid solution formation.

Irradiation of vipac mixed oxide fuel, however, produced a much more readily dissolvable material. A definite correlation between fuel burnup and dissolvability was found. For example, the undissolved residue remaining from a sample irradiated to 2900 MWD/MTM was almost fifty times greater than that from a sample irradiated to 9600 MWD/MTM. This increased dissolvability with burnup is the result of solid solution formation during irradiation and/or an irradiation enhanced dissolvability effect.

3.0 EXPERIMENTAL

All operations with irradiated and unirradiated fuels were carried out in hot cell facilities and standard plutonium gloveboxes, respectively. The use of 12 M nitric acid was chosen for consistency with both previous investigations^(1,10,13) and the Purex process. Details of the experimental procedures and fuel fabrication parameters are discussed in Section 3.1 - 3.3.4, which follow.

3.1 Dissolvability Procedure

The specially constructed apparatus shown in Figure 1, and described previously,⁽¹³⁾ was used for conducting the dissolvability studies. When necessary the apparatus was fitted with larger tubes to accomodate larger solution volumes.

The dissolvability procedure consisted of treating fuel samples with boiling 12 M nitric acid for a period of 6 hours. Treatments for periods longer than 6 hours resulted in negligible additional dissolution.

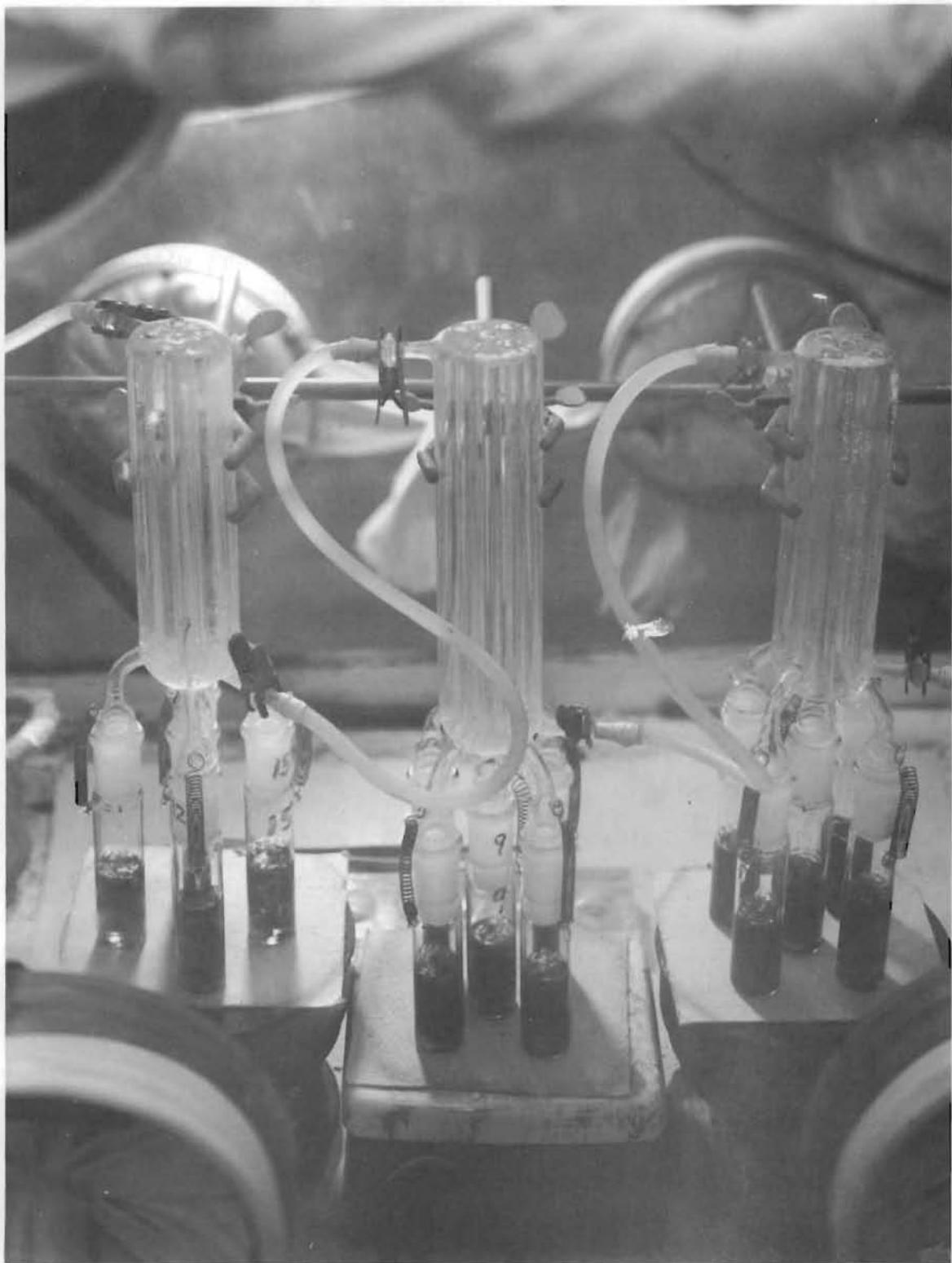


FIGURE 1. Dissolubility Apparatus

Any residue remaining after this treatment was carefully separated from the solution, dried and weighed. The residue was then dissolved in a portion of 12 M HNO₃-0.005 M HF solution and retained for subsequent analysis for uranium and plutonium content.

3.2 Dissolution Rate Procedure

The dissolution rate studies were conducted in glass vessels fitted with a water-cooled condenser and a side arm through which dissolver solutions could be withdrawn for subsequent analysis.

Dissolution rate studies were made on mixed-oxide pellets prepared from mechanically-mixed UO₂ and PuO₂ powder which had been sintered at 1650 °C for 10 hours or 1700 °C for 8 hours. The procedure employed for the rate studies consisted of adding a mixed oxide fuel pellet to sufficient boiling nitric acid to provide an acid to metal mole ratio of 30. Small samples of dissolver solution, less than 0.5 ml, were periodically withdrawn from the dissolver vessel during the course of pellet dissolution. Total volume withdrawn as samples amounted to about 2 percent of the dissolver solution present, and the volume withdrawn was not replaced with fresh acid. The samples were analyzed for uranium and plutonium content by x-ray fluorescence spectrometry and alpha counting, respectively.

3.3 Selection and Source of Fuel Elements

Sample selection was limited to previously fabricated fuel samples which were currently available at Pacific Northwest Laboratory and which were considered to be candidates for thermal recycle fuels.

3.3.1 Unirradiated Cold-Press-Sinter Mixed-Oxide Pellets

The unirradiated cold-press-sinter mixed-oxide pellet fuel chosen for the dissolubility studies represented three possible fabrication

variables: pellet pressing pressure (32,000 - 56,000 psi), sintering temperature (1650° and 1700 °C), and sintering time (6, 8, and 10 hours).

Variations in pressing pressure during pellet fabrication affect the green density (density prior to sintering) of a pellet which in turn affects shrinkage and final sintered density.⁽⁸⁾ PuO_2 powder which has been calcined at temperatures from 700° to 1600 °C is known to be sparingly soluble in boiling nitric acid.⁽¹²⁾ However, the cold-press-sinter UO_2 - PuO_2 pellet fuel the sintering temperature and time at temperature (soak time) influence the grain size, pore structure and final density of the fuel.⁽⁹⁾ In addition, the sintering temperature and time at temperature determine the extent to which single phase solid solution formation occurs in the mixed-oxide. The extent of solid solution formation has been shown to have a major effect on the dissolution of mixed-oxide fuels in nitric acid solutions.^(1,12,13) Mixed-oxide fuels with extensive solid solution formation are readily soluble in nitric acid while in mixed-oxide fuels lacking solid solution formation, the plutonium oxide fraction is relatively insoluble. In general, longer sintering times increases the dissolubility but reduce the dissolution rate of mixed oxide fuels.⁽¹²⁾

The unirradiated fuel pellets were originally prepared from ball milled United Nuclear UO_2 (ammonium diuranate process) and PuO_2 obtained by calcination of plutonium oxalate at 900 °C. The oxide powders were blended together with 2 w/o carbowax and 0.25 w/o Sterotex added as binder and die lubricant, respectively. The mixture was then dried 8 hours at 80 °C and granulated through a 20 mesh screen prior to pressing.

3.3.2 Unirradiated Vibrationally Compacted Mixed-Oxide Fuel

The unirradiated vipac mixed-oxide fuel samples were obtained from PRTR (Plutonium Recycle Test Reactor) fuel rods. The fuel in these rods was prepared by blending ceramic grade UO_2 (-65 mesh) and PuO_2 (-325 mesh) powders. The mixture was then subjected to high-energy-rate pneumatic impaction in an evacuated container heated to approximately 1000 °C. The resulting mass was crushed to produce near theoretical density UO_2 - PuO_2

particles.⁽¹⁴⁾ The sized particles (average particle size -6 mesh) were then vibrationally compacted directly into the fuel cladding tubes. A detailed comparison of pellet and vipac fuels has been previously reported.⁽¹⁵⁾

3.3.3 Irradiated Cold-Press-Sinter Mixed-Oxide Pellet Fuel

All irradiated cold-press-sinter fuel samples were taken from PRTR fuel rods. Samples were generally obtained from the midplane or peak heat rating section of each fuel rod. Samples were obtained from PRTR rods A-102 and A-103 (pellet fuels) from three different axial positions, top, center, and bottom, along the length of each rod.

3.3.4 Irradiated Vibrationally compacted Mixed-Oxide Fuel

The irradiated vipac mixed-oxide fuel samples were all prepared by the procedure outlined above except for fuel rod DB-63. Fuel rod DB-63 was prepared by vibrationally compacting ceramic grade UO_2 and PuO_2 powders which had been incrementally loaded directly into the cladding tube.

4.0 RESULTS AND DISCUSSION

The mixed-oxide fuels examined in this study exhibited wide differences in dissolubility. In general, the cold-press-sinter pellet fuels were completely dissolved after exposure to boiling 12 M nitric acid, with irradiation having little effect. The dissolubility of pneumatically-impacted, vipac mixed-oxide fuels, however, exhibited a great dependence on irradiation.

4.1 Dissolubility of Unirradiated Cold-Press-Sinter Mixed-Oxide Pellet Fuel

The results of dissolubility tests with unirradiated cold-press-sinter mixed-oxide pellet fuel are summarized in Table I. The data indicate that all the cold-press-sinter pellets examined in this study were essentially completely dissolved after a single 6-hour exposure to boiling 12 M nitric acid. Assuming that 4 moles of nitric acid per mole of oxide are required

Table I
 DISSOLUBILITY OF UNIRRADIATED UO_2 - 4 w/o
 PuO_2 COLD-PRESS-SINTER PELLET FUEL

Conditions: Six hours exposure to boiling 12 M HNO_3 , Acid/Metal mole ratio \approx 40.

<u>Pellet No.</u>	<u>Press Pressure, PSI</u>	<u>Density, % of Theoretical</u>	<u>Sintering Conditions (a)</u>	<u>Weight Percent Undissolved</u>
A-1-1	32,000	91.9	6 hrs @ 1650 °C	0.000
A-1-2	32,000	92.2	6 hrs @ 1650 °C	0.008
A-1-13	32,000	92.6	6 hrs @ 1650 °C	0.000
A-1-14	32,000	92.2	6 hrs @ 1650 °C	0.000
A-1-5	40,000	91.8	6 hrs @ 1650 °C	0.000
A-1-16	40,000	92.9	6 hrs @ 1650 °C	0.000
A-1-17	40,000	92.7	6 hrs @ 1650 °C	0.009
A-1-8	48,000	92.8	6 hrs @ 1650 °C	0.006
A-1-19	48,000	N.A	6 hrs @ 1650 °C	0.008
A-1-10	56,000	92.4	6 hrs @ 1650 °C	0.003
A-1-11	56,000	92.5	6 hrs @ 1650 °C	0.009
A-1-22	56,000	92.9	6 hrs @ 1650 °C	0.006
A-1-23	56,000	93.6	6 hrs @ 1650 °C	0.007
B-1-3	N.A	N.A	8 hrs @ 1700 °C	0.008
B-1-4	N.A	N.A	8 hrs @ 1700 °C	0.006
B-2-3 ^(b)	N.A	N.A	10 hrs @ 1650 °C	0.000
B-2-4 ^(b)	N.A	N.A	10 hrs @ 1650 °C	0.009

(a) Sintered in argon - 8% hydrogen atmosphere. Heating rate = 100 °C/hr to maximum temperature indicated (with 1 hour hold at 400 °C). Cooling rate = 100 °C/hr.

for dissolution, a large excess of acid was employed to avoid any effects due to depletion of acid strength.

None of the fabrication variables examined in this study, i.e., pressing pressure, sintering time, and sintering temperature, had a noticeable effect on dissolubility within the ranges examined. Recent studies⁽¹⁶⁾ of the interrelationships between fabrication variables and the dissolution properties of fast reactor fuels have shown, however, that all three variables do affect fuel dissolubility, with changes in sintering temperature producing the major effect. The differences in sintering temperature and time at temperature (1650 °C for 6 and 10 hours and 1700 °C for 8 hours) between the fuel pellets examined in this study were not great enough to exhibit major differences in dissolubility. Studies of the effects of sintering variables on the dissolution properties of fast reactor fuels indicates that the above variations in sintering conditions are well within the range where extensive solid-solution formation and attendant complete dissolution of the plutonium fuel fraction occurs.^(7,12,13)

4.2 Dissolution Rates of Unirradiated Cold-Press-Sinter Mixed-Oxide Pellet Fuel

The reprocessing of mixed-oxide fuel by dissolution in nitric acid without the addition of corrosive agents such as fluoride ion leads to economic advantages in dissolver construction. The design of critically safe dissolvers for reprocessing such fuels requires data on fuel dissolution rates and more importantly, on whether preferential dissolution of uranium takes place. Preferential dissolution of uranium accompanied by accumulation of undissolved plutonium would lead to criticality problems. Dissolution rate studies were performed on unirradiated sintered mixed-oxide fuel pellets to provide a reference point for subsequent dissolution rate studies with irradiated fuels. Two such studies are summarized in Table II and Figures 2 and 3.

The data in Figures 2 and 3 indicate that sintering mixed-oxide fuel pellets at 1700 °C for 8 hours produces a slightly faster PuO_2 dissolution rate than does sintering at 1650 °C for 10 hours. The data in Table II

TABLE II
DISSOLUTION RATE OF UO_2 - 4 w/o PuO_2
COLD-PRESS-SINTER PELLET FUEL IN BOILING 12 \underline{M} HNO_3 (a)

Time (min)	SAMPLE B-1 (b)		
	PuO_2 Undissolved (wt %)	UO_2 Undissolved (wt %)	U/Pu (c) In Solution
15	67.5	60.2	29.4
30	32.4	32.2	24.0
60	9.0	5.3	25.0
90	2.6	1.2	24.3
120	1.0	0.0	24.2
240	0.0	0.0	24.2

SAMPLE B-2 (d)			
	PuO_2 Undissolved (wt %)	UO_2 Undissolved (wt %)	U/Pu (c) In Solution
15	68.4	64.9	26.7
30	36.8	31.0	26.2
60	10.5	4.5	25.6
90	5.3	1.7	24.9
120	1.8	0.5	24.3
240	0.0	0.0	24.0

(a) Acid to metal mole ratio \approx 30
(b) Sintered 8 hours @ 1700 °C in Ar-8% H_2
(c) U/Pu mole ratio in pellet was 25.0
(d) Sintered 10 hours @ 1650 °C in Ar-8% H_2

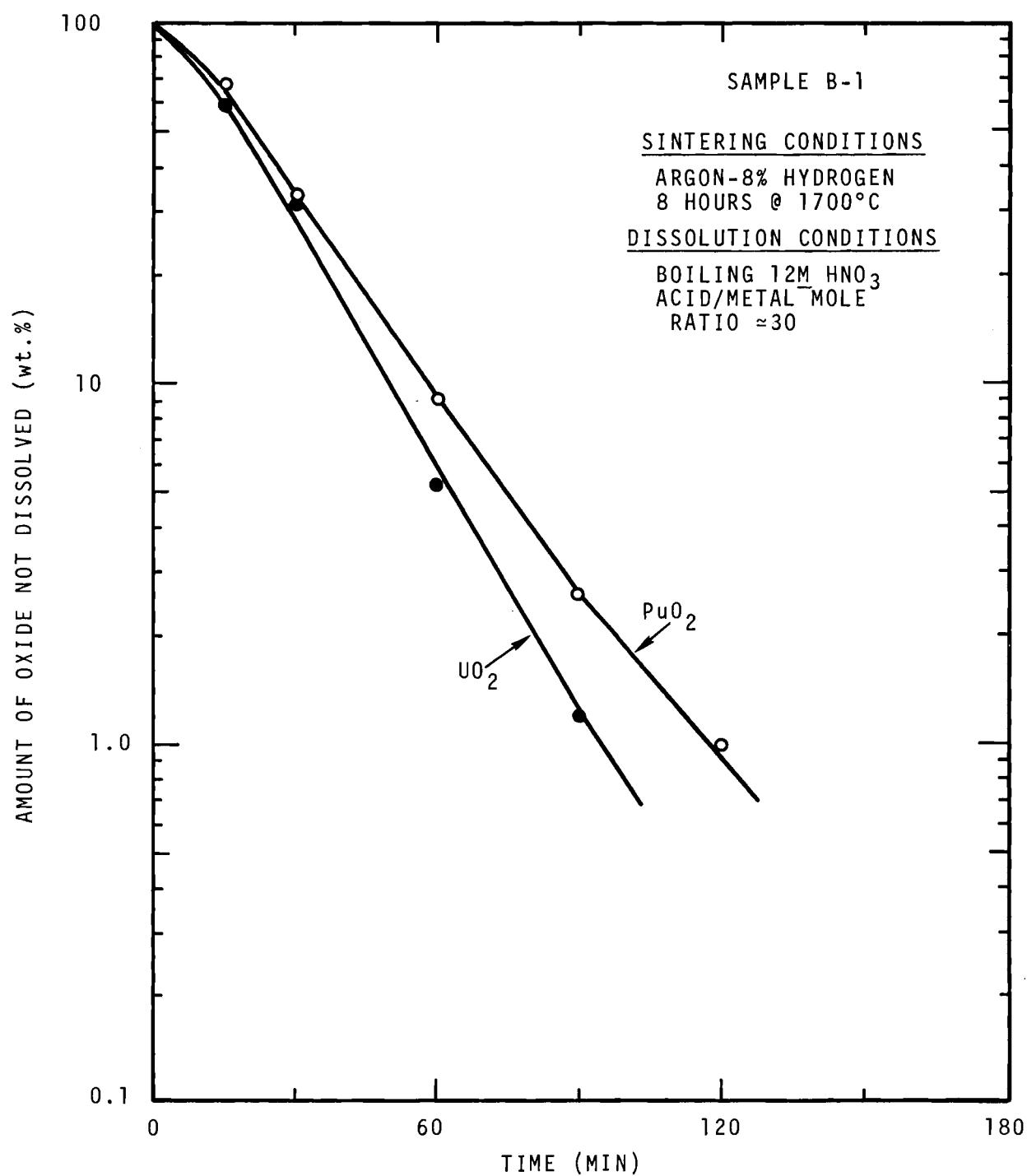


Figure 2. Dissolution Rate of UO₂-4 wt % PuO₂ Cold-Press-Sinter Pellet Fuel

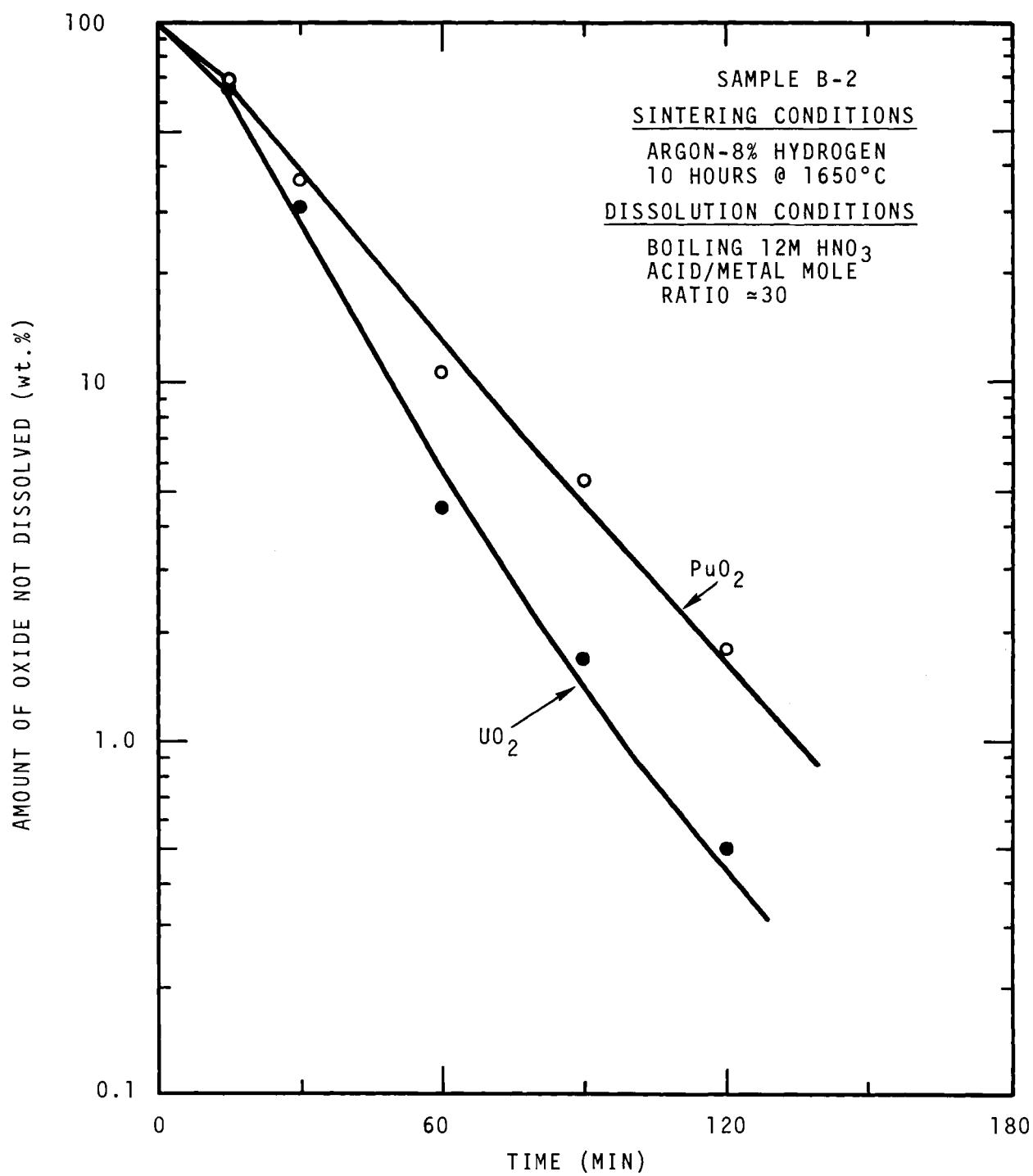


Figure 3. Dissolution Rate of UO₂-4 wt % PuO₂ Cold-Press-Sinter Pellet Fuel

show that the ratio of uranium to plutonium in solution remains relatively constant in both pellet types with relatively little preferential dissolution taking place. The ratio is more constant for the pellet sintered at 1700 °C for 8 hours because of the slightly faster PuO_2 dissolution rate of this sample.

Baehr and Dippel⁽¹²⁾ studied the effect of sintering time on the dissolution properties of fast reactor mixed-oxide fuels. They found that increased sintering times (at constant temperature of 1500 °C) resulted in increased solid solution formation and less preferential dissolution of UO_2 when the fuels were dissolved in nitric acid. Nearly stoichiometric dissolution of the mixed oxides resulted after the UO_2 -15 w/o PuO_2 fuel had been sintered 16 hours.

4.3 Dissolubility of Irradiated Cold-Press-Sinter Mixed-Oxide Pellet Fuel

Dissolubility data for irradiated mixed-oxide cold-press-sinter pellet fuels are shown in Table III. As could be expected from the previous dissolubility data on similar unirradiated fuels, the irradiated cold-press-sinter pellet fuels were essentially completely dissolved after a single 6-hour exposure to boiling 12 M HNO_3 . The samples, which were obtained from PRTR fuel rods, had received burnups ranging from 3220 MWD/MTM to 11705 MWD/MTM. Initial tests with these samples, at an acid to metal mole ratio of 40, resulted in no detectable residue. Accordingly, the sample size was increased to provide an acid to metal mole ratio of 16 which yielded the residue values shown in Table III.

Fuel samples taken from different axial positions along the lengths of fuel rods A-102 and A-103 showed no correlation between axial rod position and dissolubility.

4.4 Dissolubility of Unirradiated Vibrationally Compacted Mixed-Oxide Fuel

Dissolubility tests were made on unirradiated, pneumatically impacted, vibrationally compacted, mixed-oxide fuel containing 2 and 4 w/o PuO_2 to provide a reference point for dissolubility tests with similar irradiated

TABLE III
DISSOLUBILITY OF IRRADIATED UO_2 - PuO_2 COLD-PRESS-SINTER PELLET FUEL

Conditions: Six hours exposure to boiling 12 M HNO_3 , acid/metal mole ratio ≈ 16

<u>Fuel No. (a)</u>	<u>Composition</u>	<u>Burnup, MWD/MTM</u>	<u>Undissolved Residue, wt %</u>
ZZ-17	UO_2 - 0.5 w/o PuO_2	9207	0.000 (b)
ZZ-7	UO_2 - 0.5 w/o PuO_2	9777	0.000 (b)
ZZ-12	UO_2 - 0.5 w/o PuO_2	11705	0.000 (b)
A-102	UO_2 - 2 w/o PuO_2	3220	0.018 (c)
A-103	UO_2 - 2 w/o PuO_2	3290	0.010 (c)

(a) PRTR identification number

(b) Average of duplicate determinations

(c) Average of triplicate determinations.

vipac fuels. The dissolubility data are shown at the beginning of Table IV. A substantial portion of the plutonium oxide in these samples remained undissolved after a 6 hour exposure to boiling 12 M nitric acid. The residue remaining from one such test was dissolved in boiling 12 M HNO_3 -0.1 M HF solution. Subsequent analysis of the solution indicated that 65.4 wt % of the PuO_2 originally present in the sample had remained undissolved after the 6-hour exposure to boiling 12 M nitric acid.

These results are indicative of the lack of single phase, solid solution formation in fuels fabricated under these conditions. Schulz^(1,10) also found unirradiated vipac fuel, fabricated under similar conditions, resistant to dissolution in boiling nitric acid.

TABLE IV
 DISSOLUBILITY OF VIBRATIONALLY COMPACTED UO_2 - PuO_2 FUELS IN NITRIC ACID
 Conditions: Six hours exposure to boiling 12 M HNO_3 , acid/metal
 mole ratio ≈ 16

<u>Fuel Rod No. (a)</u>	<u>Composition</u>	<u>Burnup MWD/MTM</u>	<u>Undissolved Residue (b) wt %</u>
AB-03	UO_2 - 4 w/o PuO_2	0	2.74
2H-112	UO_2 - 2 w/o PuO_2	0	1.25 (c)
FE-69	UO_2 - 2 w/o PuO_2	2884	1.13
FE-74	UO_2 - 2 w/o PuO_2	4863	0.38
FS-07	UO_2 - 2 w/o PuO_2	9176	0.13
FR-78	UO_2 - 2 w/o PuO_2	9630	0.024
DF-80	UO_2 - 1 w/o PuO_2	11500	0.028
DB-63 (d)	UO_2 - 0.5 w/o PuO_2	18500	0.006

(a) PRTR identification number

(b) Average of duplicate determinations

(c) Analysis of residue indicated that 65.4% of PuO_2 originally present remained undissolved.

(d) Fabricated from incrementally loaded UO_2 and PuO_2 ceramic grade powders. All remaining fuel rods fabricated from mechanically mixed UO_2 - PuO_2 particles consolidated by high-energy-rate pneumatic impaction.

Vipac fuels fabricated from coprecipitated, fused, or sintered and crushed UO_2 - PuO_2 feed material could be expected to exhibit dissolution properties similar to cold-press-sinter pellet fuels.

4.5 Dissolubility of Irradiated Vibrationally Compacted Mixed Oxide Fuels

The results of dissolubility tests on irradiated vipac mixed-oxide fuel rod samples are summarized in Table IV. An apparent correlation between dissolubility and peak fuel burnup for UO_2 - 2 w/o PuO_2 vipac fuel samples

is depicted graphically in Figure 4. Schulz⁽¹⁾ has previously suggested that significant in-reactor conversion of UO_2 - PuO_2 oxide mixtures to solid solution occurs during fuel irradiation. The data shown in Figure 4 appear to confirm this. The correlation between peak burnup and dissolubility reflects the extent of solid solution formation in the mixed-oxide fuel during exposure to elevated temperatures for varying lengths of time. If so, then the extent of solid solution formation and hence dissolubility is more sensitive to fuel temperature or power (KW/ft) than it is to peak burnup. The effects of sintering times and temperature on unirradiated fuels would tend to bear this out. Unfortunately, fuel element power level computations and fuel element time-at-temperature data were not available for the fuel rods used in this study.

4.6 Ceramographic Correlations

Ceramographic examination (photomacrographs, beta-gamma autoradiographs and alpha autoradiographs) are useful aids in determining the operating conditions of a fuel rod during irradiation. Ceramographic examinations of two of the vipac UO_2 - 2 wt % PuO_2 fuel samples tested are shown in Figure 5. Striking structural differences are exhibited in the photomacrographs of fuel element FE-69 (peak burnup = 2884 MWD/MTM) and fuel element FR-78 (peak burnup = 9630 MWD/MTM). The lack of noticeable in-reactor fuel restructuring in rod FE-69 indicates that this rod operated at a relatively low linear heat rating (≈ 6.3 KW/ft) with attendant peak fuel temperatures estimated to be about 1000 °C. In contrast, fuel element FR-78 exhibits an extensive region of columnar grain growth which is indicative of the substantially higher linear heat rating (≈ 2600 °C) that existed in the rod.⁽¹⁷⁾ This region of columnar grain growth is caused by rapid pore migration of the thermal gradient toward the center of the fuel by a continuous vaporization-condensation process which results in complete solid solution formation. The fuel density increases from about 85% to over 95% of theoretical in the region of columnar grain growth. This fuel densification, which commences at

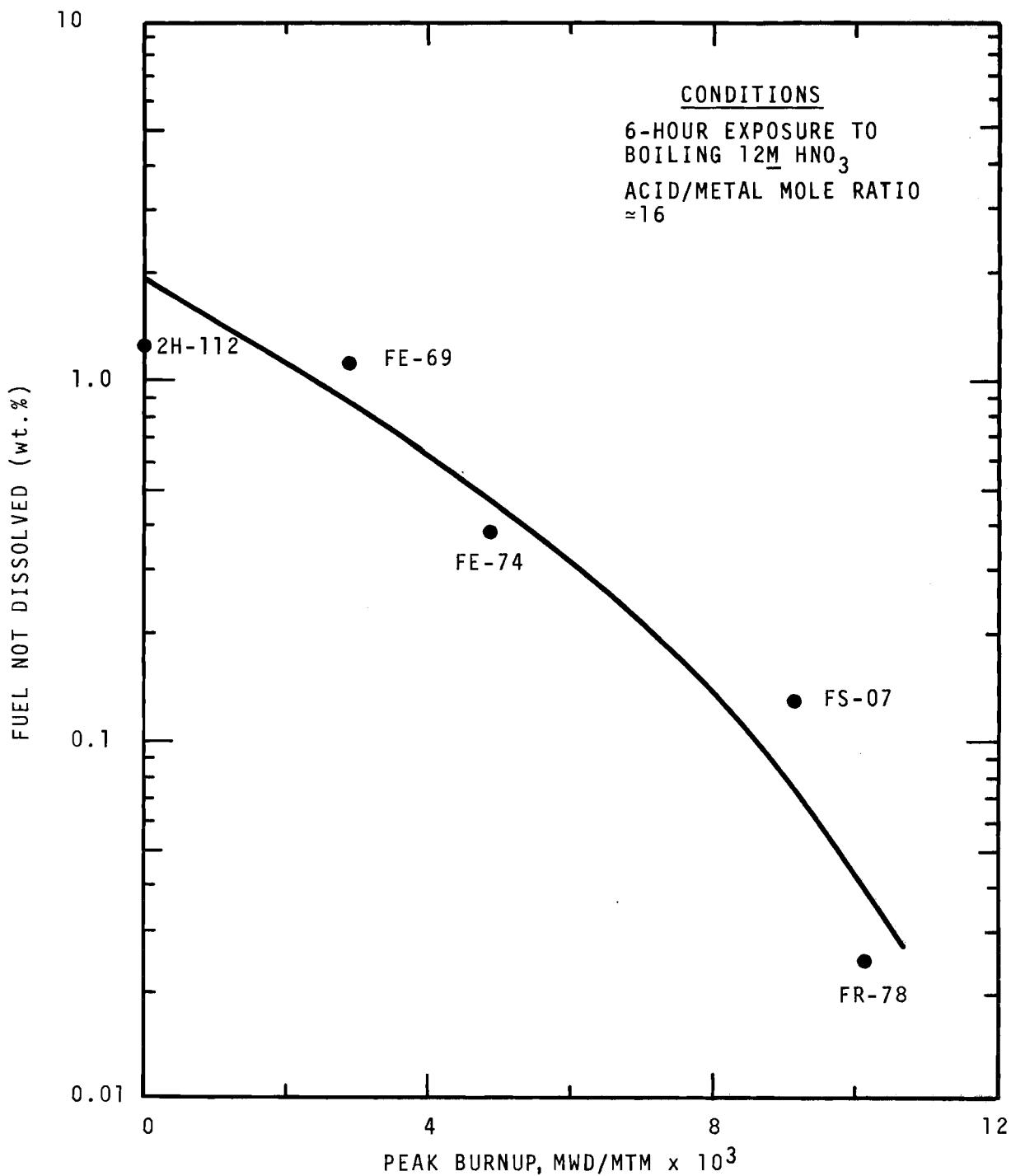


Figure 4. The Effect of Peak Burnup on the Dissolubility of
Vipac UO_2 -2 wt % PuO_2 Fuels

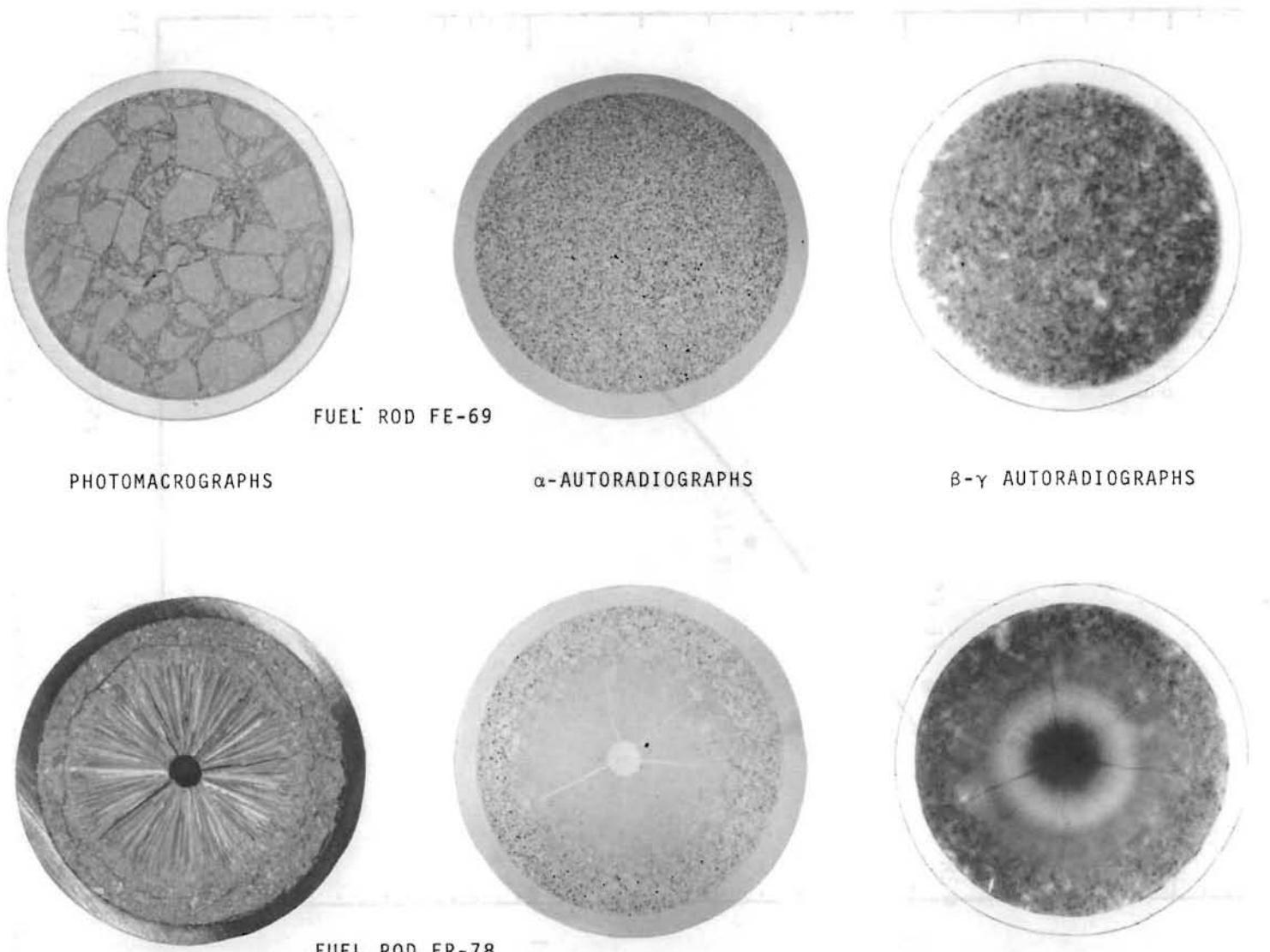


Figure 5. Transverse Sections From Vibrationally Compacted Mixed-Oxide Fuel Rods Irradiated in PRTR.

about 1700 °C, causes a characteristic void to form in the center of the fuel rod.⁽¹⁵⁾

Solid solution formation occurs rapidly in those portions of vipac mixed-oxide fuel rods operating at columnar grain growth temperatures, i.e., > 1800 °C. However, the increased dissolubility of irradiated vipac fuel does not appear to be confined to that portion of the fuel cross section exhibiting columnar grain growth. Estimation of the amount of undissolved residue expected from samples of fuel rod FR-78, assuming the area of the fuel without columnar grain growth is equivalent to unirradiated fuel, results in a calculated residue weight which is significantly greater (30X) than that which was found experimentally. Thus, it appears that dissolubility is also increased in the peripheral fuel region surrounding the region of columnar grain growth in irradiated vipac mixed-oxide fuels. Whether this increased dissolubility is an effect of in-reactor thermal sintering, irradiation per se, or a combination of the two is not clear.⁽¹⁷⁾

5.0 CONCLUSIONS

As a result of this study, the following conclusions were made regarding the dissolution properties of UO_2 - PuO_2 thermal reactor fuels:

- o Sintering unirradiated UO_2 - 4 wt % PuO_2 cold-press-sinter pellet fuel for 6-10 hours at 1650-1700 °C results in sufficient solid solution formation to render the fuel readily soluble in boiling 12 M nitric acid.
- o Unirradiated UO_2 - 4 wt % PuO_2 cold-press-sinter pellet fuel exhibited no direct correlation between pressing pressure and dissolubility for pressures in the range 32,000 - 56,000 PSI.
- o Cold-press-sinter mixed-oxide pellet fuel which had been irradiated to a maximum burnup of 11,700 MWD/MTM was readily soluble in boiling 12 M nitric acid.

- o Little or no preferential dissolution of UO_2 occurred when unirradiated UO_2 - 4 wt % PuO_2 cold-press-sinter pellet fuel, which had been sintered 6-10 hours at 1650 - 1700 °C, was exposed to boiling 12 M nitric acid.
- o In unirradiated mechanically mixed, pneumatically impacted, vipac fuel containing UO_2 - 2 wt % PuO_2 , between 60 and 70% of the PuO_2 remained undissolved after a 6-hour exposure to boiling 12 M nitric acid.
- o Irradiation of pneumatically impacted, vipac mixed-oxide fuel resulted in a much more readily dissolvable material, with a definite correlation existing between burnup and dissolubility.
- o The enhanced dissolubility of irradiated pneumatically impacted, vipac mixed-oxide fuels was not limited to the area of the fuel exhibiting columnar grain growth.

6.0 ACKNOWLEDGEMENTS

The authors gratefully acknowledge the suggestions of W. W. Schulz of the Atlantic Richfield Hanford Company. Special thanks to M. D. Freshley for his assistance in obtaining fuel samples and providing background for the section on ceramography and to Dr. R. L. Moore (currently employed by the WADCO Corporation) and L. D. Perrigo under whose direction this work was performed.

REFERENCES

1. W. W. Schulz, Aqueous Decladding and Dissolution of Plutonium Recycle Test Reactor Fuels, Part 2: PuO₂-UO₂ Fuels, BNWL-204PT2. Pacific Northwest Laboratory, Richland, Washington, November, 1966.
2. W. S. Gilman, A Review of the Dissolution of Plutonium Dioxide, Part II, MLM-1513, Mound Laboratory, Miamisburg, Ohio, August 1968.
3. J. H. Goode, Hot Cell Dissolution of Highly Irradiated 20% PuO₂ - 80% UO₂ Fast Reactor Fuel Specimens, ORNL-3754. Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 1965.
4. R. F. Maness, Corrosion of 304-L Stainless Steel and HAPO-20 In Acid Fluoride Systems, HW-80658. General Electric Company, Richland, Washington, January 1965.
5. P. D. Miller, E. F. Stephan, W. E. Berry and W. K. Boyd, Corrosion of Construction Materials in Boiling 13 M Nitric - 0.1 M Hydrofluoric Acids, BMI-X-434. Battelle Memorial Institute, Columbus, Ohio, 1967.
6. K. J. Schneider, editor. Waste Solidification Program, Volume I, Process Technology - Pot, Spray and Phosphate Glass Solidification Processes, BNWL-1073. Pacific Northwest Laboratory, Richland, Washington, August 1969.
7. L. E. Russell, N. H. Brett, J.D.L. Harrison and J. Williams, "Observations on Phase Equilibria and Sintering Behavior in the PuO₂-UO₂ System," Journal of Nuclear Materials, Vol. 5, pp. 216-227, 1962.
8. T. D. Chikalla, "Studies on the Oxides of Plutonium," Plutonium 1960, edited by E. Grison, W.H.B. Lord, R.D. Fowler, Cleaver-Hume Press, London, 1961. pp. 455-488.
9. I. D. Thomas, "Plutonium Ceramic Fuel Fabrication." Plutonium Handbook, edited by O. J. Wick. Gordon and Breack Publishers, New York, 1967, Volume II, pp. 619-639.

10. W. W. Schulz, Nitric Acid Dissolution of PRTR PuO₂-UO₂ Fuels, BNWL-CC-1103. Pacific Northwest Laboratory, Richland, Washington, February 1967.
11. A. L. Uriarte and R. H. Rainey, Dissolution of High-Density UO₂, PuO₂ and UO₂-PuO₂ Pellets in Inorganic Acids, ORNL-3695. Oak Ridge National Laboratory, Oak Ridge, Tennessee, April, 1965.
12. W. Baehr and Th. Dippel, On the Dissolution of Breeder Fuels Containing PuO₂ in Nitric Acid for Aqueous Reprocessing by The Purex Method, KFK 673. Available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia as report number EURFNR-471, July 1967.
13. R. E. Lerch and G. F. Schiefelbein, The Effect of Fabrication Variables on the Dissolubility of Unirradiated Mechanically Blended Mixed Oxide Fast Reactor Fuel, WHAN-FT-34. Hanford Engineering Development Laboratory, Richland, Washington, December, 1970.
14. D. W. Brite and C. A. Burgess, "High Energy Rate Pneumatically Impacted UO₂-PuO₂ Fuels," Transactions of the American Nuclear Society, Vol. 7, No. 2, 1964, p. 408.
15. M. D. Freshley, A Comparison of Pellet and Vipac Nuclear Fuels, BNWL-SA-3466, Pacific Northwest Laboratory, Richland, Washington, July, 1970.
16. R. E. Lerch and G. F. Schiefelbein, Dissolution of Unirradiated Mechanically Blended Mixed Oxide Fast Reactor Fuel, HEDL-SA-131.
17. M. D. Freshley, Private communication, Pacific Northwest Laboratory, Richland, Washington.

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