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HOT-CELL DISSOLUTION OF HIGHLY IRRADIATED 20% PuO_2--80% UO_2 FAST-REACTOR FUEL SPECIMENS

J. H. Goode

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

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J. H. Goode

OCTOBER 1965

OAK RIDGE NATIONAL LABORATORY
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CONTENTS

Page

Abstract 1

1. Introduction 1

2. Source of the Fuel Elements and Summary of Relevant Chemistry . 2

3. Acknowledgement 3

4. Experimental 4

4.1 Fuel Fabrication and Irradiation History 4

4.2 Procedure 7

4.3 Cladding Removal with Sulfuric Acid 7

4.4 Dissolution of Swaged and Pelleted 80% UO_2--20% PuO_2 in Nitric Acid 10

4.4.1 Dissolution Rates 10

4.4.2 Fission-Product Solubility 13

4.4.3 Insoluble Residues 14

4.4.4 Change in Isotopic Composition of Fuel as a Function of Irradiation 15

5. Discussion and Conclusions 18

5.1 Decladding Losses 18

5.2 Dissolution Rates 19

5.3 Fission Product Solubility and Dissolution Residues 19

6. References 20

HOT-CELL DISSOLUTION OF HIGHLY-IRRADIATED 20% PuO_2--80% UO_2 FAST-REACTOR FUEL SPECIMENS

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ABSTRACT

Hot-cell studies were made at ORNL on prototype fuel specimens to define possible problems in the head-end step in processing fuel from a Fast Breeder reactor. The fuel consisted of stainless-steel-clad PuO_2-UO_2 (20%--80%), swaged or pelletized, made and irradiated by General Electric's Vallecitos Atomic Laboratory. The irradiation levels were as high as 99,000 Mwd/metric ton.

It was found that shearing the elements into short pieces and dissolving the core with nitric acid was preferable to chemical decladding with sulfuric acid solutions because of excessive (1.5%) losses of uranium and plutonium. Also, about 60% of the fission-product cesium dissolved in the sulfuric acid; the decay heat from this cesium could cause problems in waste management. More than 99% of the PuO_2-UO_2 dissolved in less than 5 hr in all concentrations of nitric acid greater than 3 M. No fluoride was needed to accelerate the reaction, which is a distinct advantage. Undissolved residues consisted of core oxides and fission-product Mo, Zr, Pd, Ru, and Rh. Feed clarification would be required to remove these solids prior to final recovery of the fissile material by solvent extraction.

INTRODUCTION

The recovery of fissile materials from the spent fuel of proposed reactors should be studied as soon as a definite design has been established, since unforeseen problems in fuel reprocessing might alter the economics of the fuel cycle. These problems, which would affect the choice of a head-end process for preparing fuel for purification by solvent extraction, include dissolubility of irradiated fuel in nitric acid systems, losses of uranium and plutonium during processing, the effect of burnup on dissolving rates of the fuel, the solubility of high concentrations of fission products under process conditions, the amount and composition of insoluble residues, radiation effects on process chemistry, and corrosion problems.

The work outlined in this report illustrates the usefulness of preliminary investigations in the development of a head-end process. For example, it was found that chemical decladding of the fuel under study (20% PuO_2--80% UO_2, clad in stainless steel) is impractical. The losses of uranium and plutonium to the decladding solution are too high. Significantly and favorably, it was learned that it was unnecessary to use a fluoride catalyst in the nitric acid to help dissolve (leach) the fuel oxides used in these tests. Indeed, they dissolved rapidly even in dilute acid. Some caution is necessary in this regard, however, since the dissolubility of PuO_2-UO_2 mixtures is a function of fabrication.[1] Plutonium oxide is not soluble in nitric acid unless it is combined with UO_2 in solid solution.

2. SOURCE OF THE FUEL ELEMENTS AND SUMMARY OF RELEVANT CHEMISTRY

The General Electric's Vallecitos Atomic Laboratory (GE-VAL), under the sponsorship of the U.S.A.E.C., has undertaken the development of an oxide-fueled fast reactor employing 20% PuO_2--80% UO_2 fuel elements clad in stainless steel. Forty prototype fuel specimens, containing either swaged or pelleted PuO_2-UO_2, were fabricated and irradiated to burnups ranging from 5,000 to 99,000 Mwd/metric ton and at heat fluxes ranging from 0.5×10^6 to 1.6×10^6 Btu hr^{-1} ft^{-2}.[2,3] Following the postirradiation physical and metallographic examination of the specimens,[3] GE-VAL supplied the ORNL Chemical Technology Division with the sectioned remains of the prototypes for these fuel-processing studies.

Data on the dissolution of PuO_2-UO_2 fuel are rather sparse. Blanco and Watson, reporting on the dissolution of PuO_2 in the ORNL Metal Recovery Plant, stated that 52 hr were required to completely dissolve PuO_2 in boiling 10-12 M HNO_3 made 0.02 M in HF, and that it was nearly "insoluble" without the fluoride.[4] Summary papers by Russell[5] and Culler and Blanco[6] report the work of Cashin[7] at Knolls Atomic Power Laboratory. Cashin found that mixed crystals (solid solution) of PuO_2-UO_2, having an atom ratio of 1:5, respectively, which were irradiated to 5 and 35% depletion of the plutonium, dissolved completely in boiling 60% HNO_3 without fluoride

in 3 to 5 hr. Russell also mentioned the work of N. H. Brett et al., of AERE, who found that high-fired PuO_2 and PuO_2-rich solid solutions were insoluble in boiling 8 M HNO_3, while UO_2 and UO_2-rich solid solutions were completely soluble.

Uriarte and Rainey, at ORNL, studied the dissolution of unirradiated, high-density UO_2, PuO_2, and UO_2-PuO_2 and found that mixed oxides containing as much as 35% PuO_2 could be dissolved in boiling nitric acid alone provided that the PuO_2 was in solid solution in the UO_2.[1] They also derived equations for calculations of instantaneous dissolution rates of solid solutions of the mixed oxides.

Cleveland et al., at GE-VAL, prepared the PuO_2-UO_2 for these prototype Fast Breeder fuel specimens as a solid solution by coprecipitation of uranium and plutonium from nitrate solutions with ammonium hydroxide and subsequent reduction with hydrogen.[2] Gerhart, also of GE-VAL, indicated that fine particles of the irradiated fuel specimens used in these experiments were completely dissolved for burnup analysis in 12 M HNO_3 by warming to 60°C.[8] However, the work here was with pelleted or swaged coprecipitated oxides, not powders.

3. ACKNOWLEDGEMENT

I wish to acknowledge the invaluable assistance of J. W. Ullmann, of the Chemical Technology Division Long-Range Planning Group, in negotiating for the irradiated specimens from GE-VAL. H. W. Alter, S. C. Furman, J. M. Gerhart, and K. Kelty of GE-VAL, and G. C. Banick, of GE at Oak Ridge, arranged for transfer of the specimens and supplemental information. R. H. Rainey assisted in the initial planning of the hot-cell experiments, which were conducted by technicians R. C. Shipwash and G. E. Woodall. Mr. Jorgen Klitgaard, of the Danish Atomic Energy Commission, on loan to Oak Ridge National Laboratory from the Eurochemic Company, Mol, Belgium, assisted in supervising the experiments. Ionic analyses were performed by the groups of J. H. Cooper and C. E. Lamb, spectrography by W. R. Musick, mass-spectrometry by J. R. Sites, and radiochemistry by E. I. Wyatt.

4. EXPERIMENTAL

4.1 Fuel Fabrication and Irradiation History

As noted above, the fuel for the experimental capsules was prepared by coprecipitating the plutonium (IV) and uranium (VI) from a nitrate solution with ammonium hydroxide. The precipitate was dried and reduced to the oxide in a hydrogen-nitrogen atmosphere at 900°C. The oxide was then ground and separated into two size fractions, -140 to +300 mesh and -300 mesh. The larger particles were sintered in a hydrogen-helium atmosphere at 1400°C and loaded into tubes for swaging to 75% of theoretical density. The -300 mesh oxide was pressed into pellets (0.149 in. in diameter and 0.250 in. long) and sintered at 1700°C in a hydrogen-helium atmosphere to about 95% of theoretical density. Details of the fuel and specimen fabrication procedure are described in ref 2. Since the final oxides were soluble in nitric acid, it is assumed that they were present as a true solid solution in the crystalline state. Figure 1 shows schematic diagrams of the stainless-steel-clad specimens. (Note the normal-enrichment UO_2 insulator pellets at the ends of the specimens.)

The 10 capsules, containing 40 fuel specimens, were irradiated in the General Electric Test Reactor (GETR) for various times during 1960. Full details are described in ref 3. Burnups and fuel exposure were obtained from thermocouple data on the average heat flux per specimen, surface area, reactor exposure time, fuel weight, postirradiation gamma scanning, and heavy-element and radiochemical analyses of selected specimens. The experimental parameters for all specimens were:

Burnup: 4,700 to 99,000 Mwd/metric ton of uranium and plutonium
Heat flux: 0.5 to 1.68 x 10^6 (max), 0.4 to 1.3 x 10^6 (avg) Btu hr^{-1} ft^{-2}
Surface temperature of cladding: 790 to 1260 (max), 590 to 1060 (avg) °F.

Postirradiation examination of each test specimen (done at GE-VAL) included visual examination; removing NaK from the outer capsules; gamma scanning; puncturing, collecting, and measuring fission gases; sectioning the fuel specimens and measuring central voids; photographing exposed fuel sections; and detailed metallographic examination of sections. Figure 2 shows a typical sectioning diagram obtained during the postirradiation examinations.

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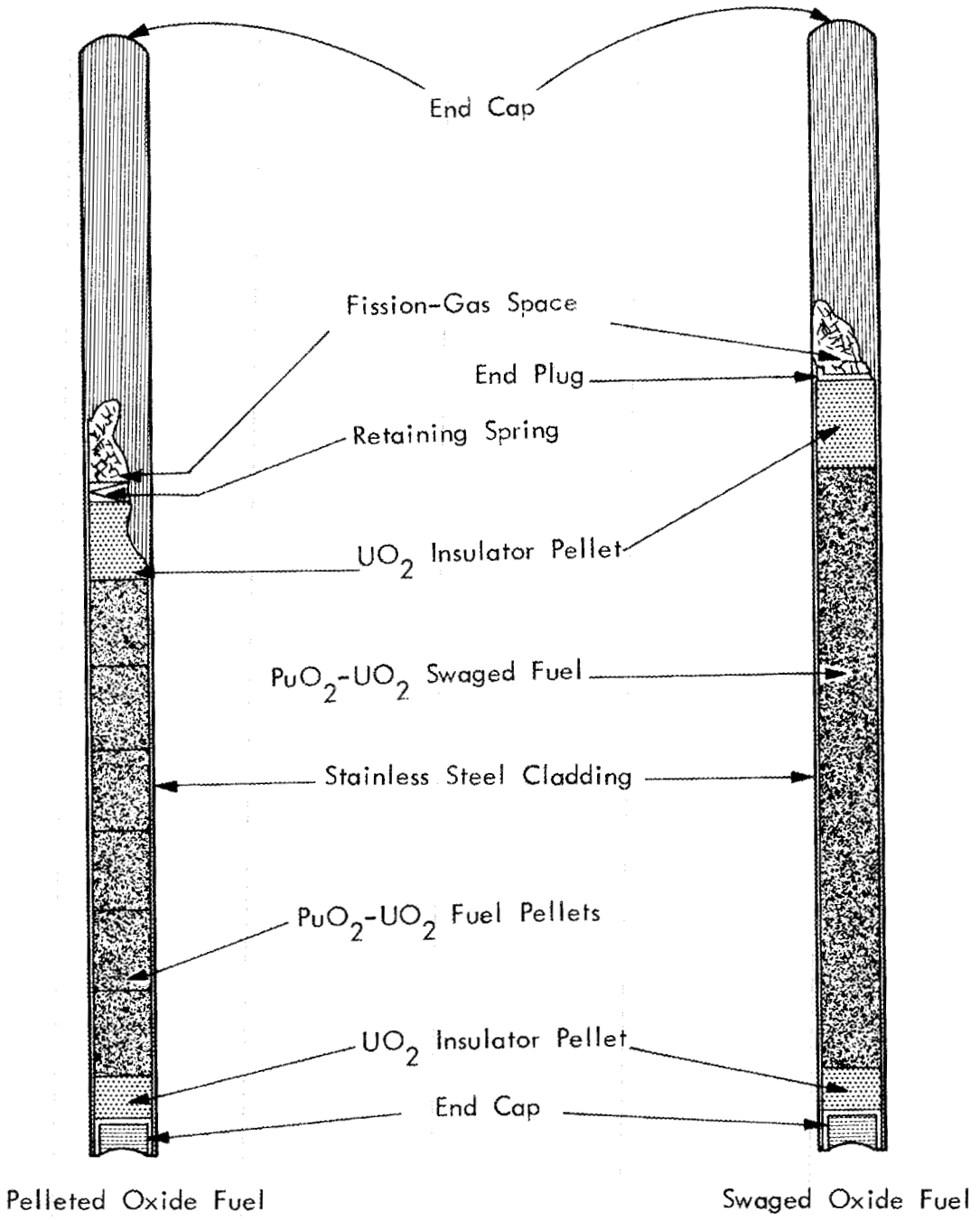

Fig. 1. Typical Fast-Breeder Specimens.

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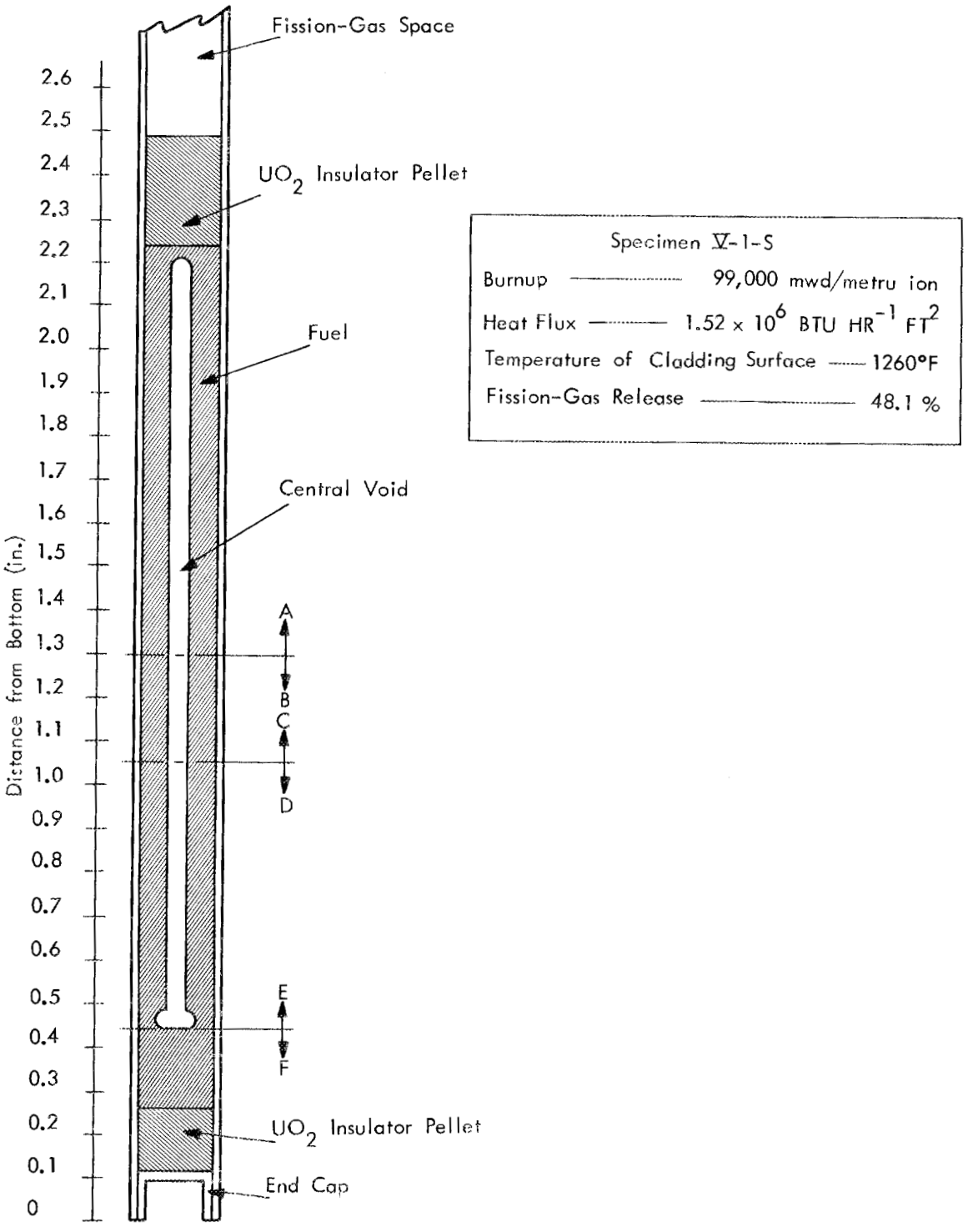

Fig. 2. Sectioning Diagram for Specimen V-1-S.

Central voids were observed in all but four of the specimens. Data on swaged specimens indicated that these voids appeared at a heat flux of 0.50 to 0.57 Btu hr^{-1} ft^{-2}; no such relationship was found for pelleted fuel. Large columnar grains surrounding the voids indicated that the mechanism of formation was grain growth brought about by sintering and/or vaporization and redeposition, rather than by melting. Most of the specimens showed radial and circumferential cracking, but no fragmenting.

Formation of fission-gas bubbles within the fuel grains was indicated by a spongy structure in the fuel, similar to that observed when UO_2 is irradiated under high-performance conditions.[9]

Table 1 summarizes the history of the specimens before they were sent to ORNL for studies and evaluations of possible head-end processing.

4.2 Procedure

Two head-end processes were tried here: (1) removing the stainless steel cladding by dissolving it in boiling 6 M H_2SO_4 (Sulfex Process), followed by dissolving the mixed-oxide fuel in nitric acid; and (2) leaching the fuel from the sectioned cladding with nitric acid to simulate the "Shear-Leach" head-end step in fuel reprocessing.[4] Losses of uranium and plutonium to the sulfuric acid solution of the cladding were determined for each specimen declad by the Sulfex process. At the end of the leaching experiments, the empty, washed, stainless steel cladding was dissolved in sulfuric acid to determine losses of uranium or plutonium.

The leaching experiments were made at a relatively constant volume and acidity by adding nitric acid after each rate-study sample had been removed. Where possible, individual fuel pellets (UO_2-PuO_2) were dissolved separately from the UO_2 insulator pellets in order to simplify the experiments.

4.3 Cladding Removal with Sulfuric Acid

The weighed specimens (Fig. 3) were placed in sufficient 6 M H_2SO_4 to result in a 100-g/liter solution of stainless steel, and then refluxed for 3 or 4 hr to dissolve the cladding. The cladding on all specimens

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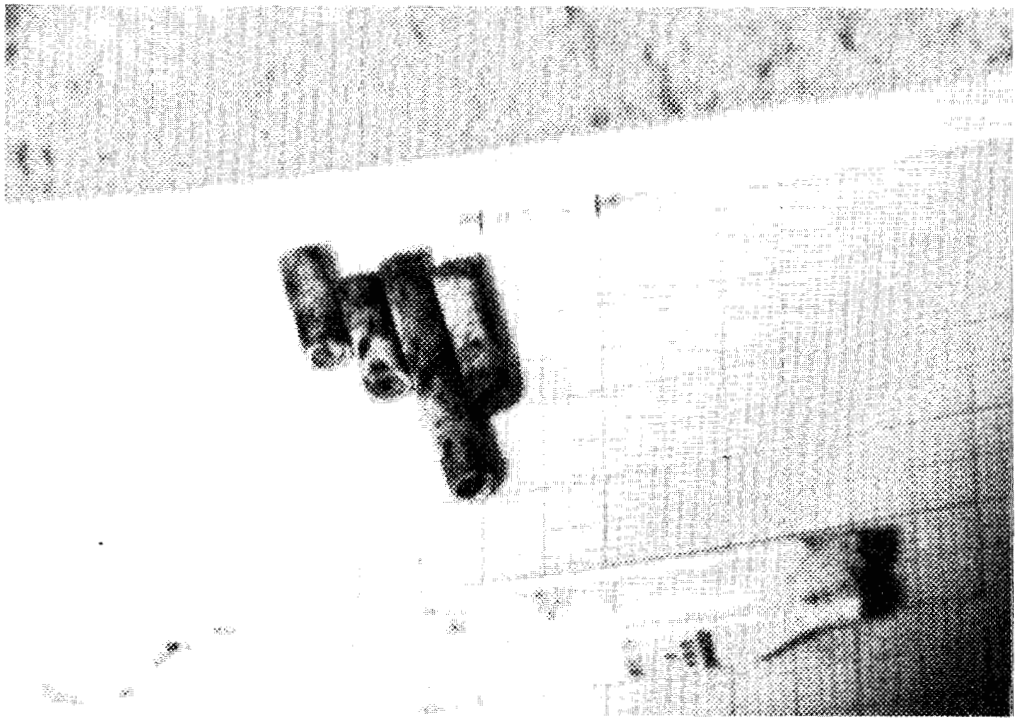

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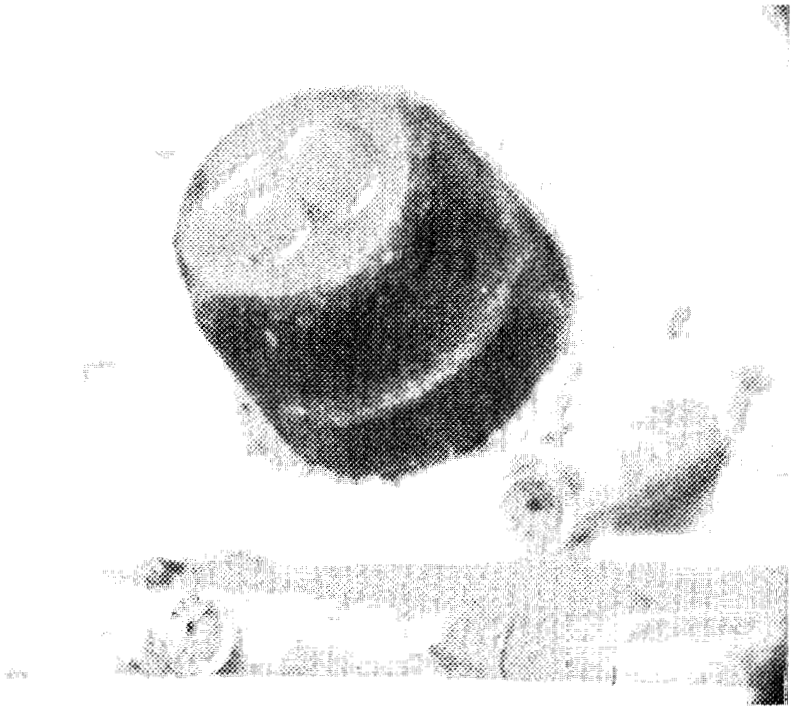

Fig. 3. Sectioned Specimens Before Decladding or Leaching.

Table 1. Reactor Histories and Densities of the Oxide Fuel Used in the Leaching Experiments.

Specimen Number[a]	Burnup (Mwd/metric ton)	Discharge Date	Density Before Irrad. (% Theor.)	Heat Flux (Btu hr^{-1} ft^{-2})	Cladding Temp. (°F)	Fission Gas Release (%)
IV-3-P	10,900	7-22-60	89.0	0.69	990	52.4
III-3-P	15,100	7-22-60	92.3	1.02	820	56.1
VII-3-P	38,900	11-5-60	96.0	1.24	1080	44.0
VI-2-P	41,600	12-11-60	96.0	0.79	1060	37.4
IX-1-P	47,600	11-5-60	86.5	1.23	1030	--
VII-2-P	49,900	11-5-60	94.7	1.50	1170	44.2
V-3-P	54,400	12-11-60	94.5	1.28	1130	38.3
V-2-P	77,400	12-11-60	95.8	1.58	1180	28.8
IV-4-S	9,000	7-22-60	75	0.53	880	27.8
VIII-4-S	19,300	11-5-60	75	0.50	820	71.3
X-1-S	36,300	11-5-60	75	0.91	--	31.1
V-4-S	42,700	12-11-60	75	0.86	930	71.7
VIII-1-S	45,000	11-5-60	75	1.07	1180	66.4
VI-1-S	69,100	12-11-60	75	1.00	1140	48.2
VII-1-S	70,200	11-5-60	75	1.44	1220	36.1
V-1-S	99,000	12-11-60	75	1.52	1260	48.1

[a]P denotes pelletized fuel; S denotes swaged fuel.

reacted with the acid at about 105°C, and no "passive" stainless steel was seen. At the end of the reaction, the solution was cooled and filtered, and the exposed fuel was washed with an equal volume of water, which was mixed with the decladding solution to form a stable solution. The filtrate was analyzed for uranium, plutonium, iron, gross gamma emitters, total Cs and ^{137}Cs gamma emission for inclusion with other ^{137}Cs in burnup analysis. The washed oxide was dried with acetone, weighed, and segregated into UO_2 or UO_2-PuO_2 portions for dissolution (Figs. 4a and 4b).

The results of the analysis of a typical decladding solution, from capsule X-1-S, were:

U -- 0.215 mg/ml
Fe -- 25.35 mg/ml
Gross alpha emitters -- 6.88×10^6 counts min^{-1} ml^{-1}
Pu alpha emission -- 5.91×10^6 counts min^{-1} ml^{-1}
Gross gamma emitters -- 5.81×10^8 counts min^{-1} ml^{-1}
Cs gamma emission -- 4.58×10^8 counts min^{-1} ml^{-1}
Ru gamma emission -- 1.04×10^6 counts min^{-1} ml^{-1}

These quantities represented 1.18% of the total uranium, 1.86% of the plutonium, and 47.2% of the cesium in the portions of the capsule involved. Table 2 shows the amounts of uranium, plutonium, and cesium found in the decladding solutions.

4.4 Dissolution of Swaged and Pelleted 20% PuO_2--80% UO_2 in Nitric Acid

4.4.1 Dissolution Rates

Dissolution rates for irradiated swaged and pelleted 20% PuO_2--80% UO_2 in 3.5 to 10 M HNO_3 are plotted in Fig. 5. Fluoride was not used in most of the dissolvents since it was found to be unnecessary.

Both the swaged and the pelleted oxides dissolved over 5 times faster than unirradiated PuO_2-UO_2 at acid concentrations greater than 3 M, i.e., >5 mg min^{-1} cm^{-2}. No major difference could be found in the rates based on the preirradiation density of the oxides. Also, the irradiation level apparently had no effect on the rates, nor did the acid concentration. The rate "difference" for leaching is due to the smaller area of oxide exposed to the dissolvent, not due to any other property.

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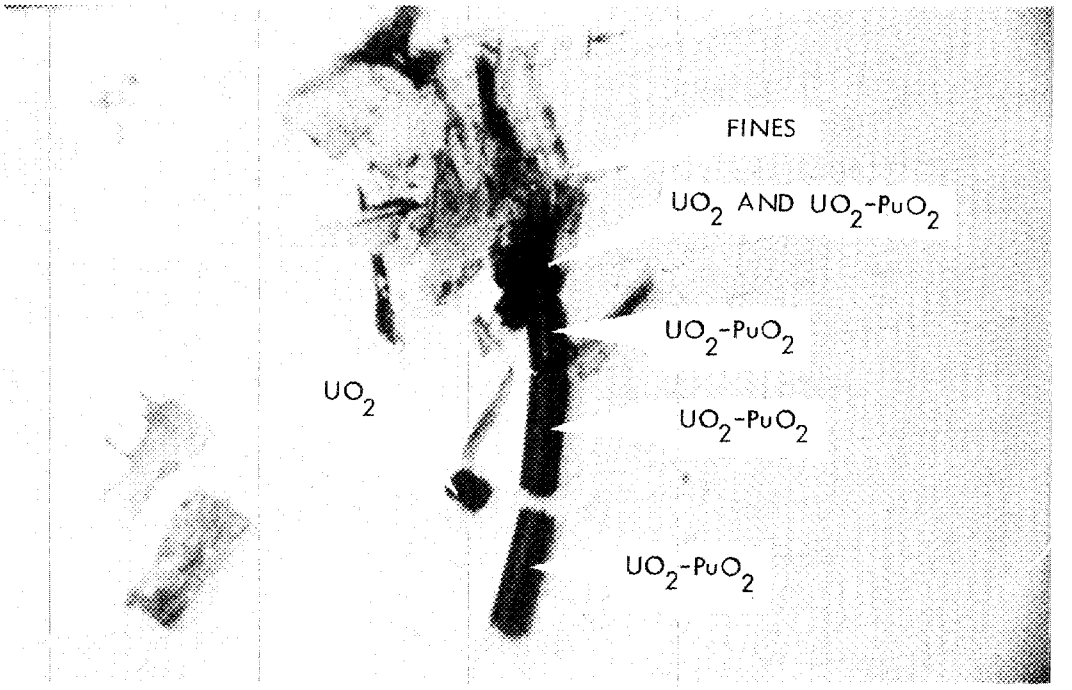

(a)

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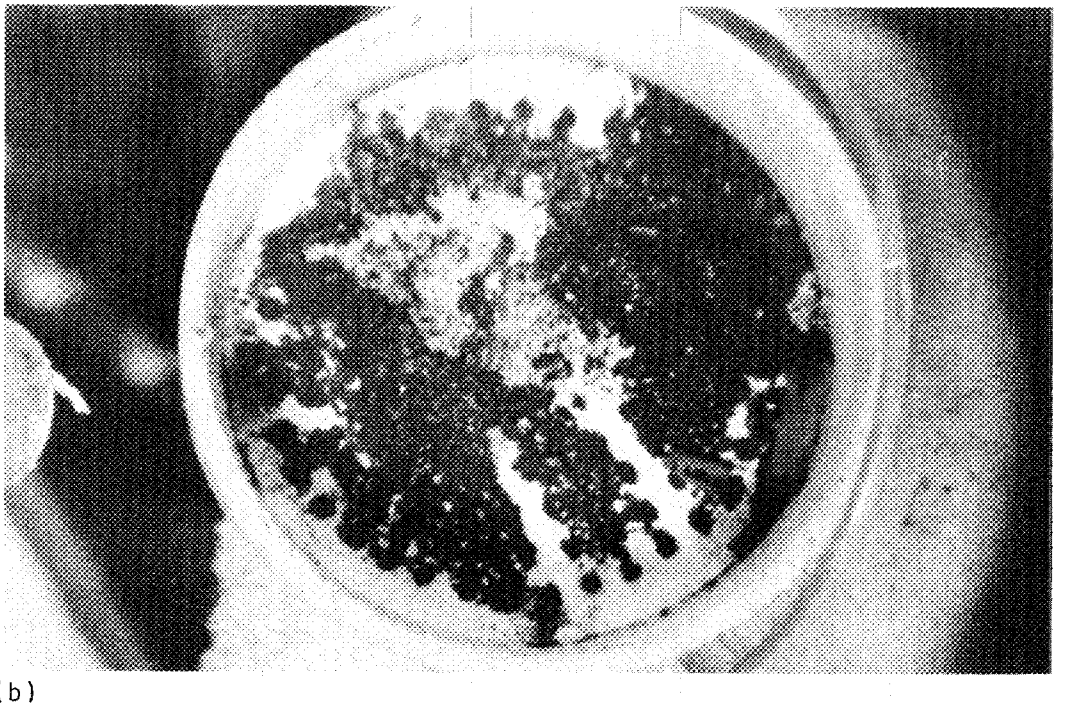

(b)

Fig. 4. Declad UO_2 and UO_2-PuO_2 from Fast-Breeder Specimens. (a) Fused fragments from capsule VII-3-p. (b) Powdered oxide and cladding remnants from X-1-S.

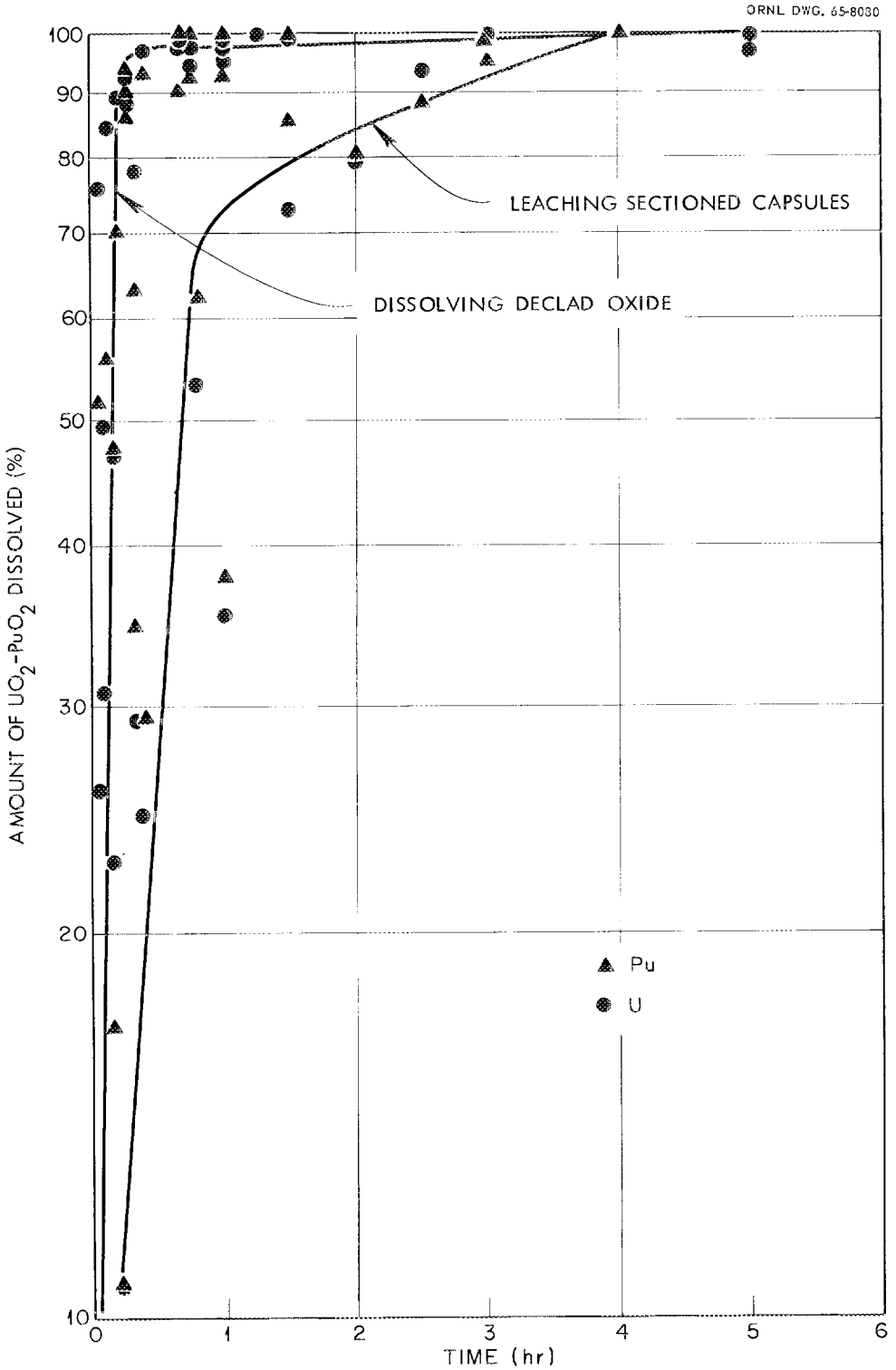

Fig. 5. Dissolving Rate of Both Swaged and Pelletized Fuel Oxides in 3.5 to 10 M HNO_3. Burnup: 9000 to 99,000 Mwd/metric ton.

Table 2. Uranium, Plutonium, and Cesium Content of Sulfex Decladding Solutions

Specimen Number	Burnup, Mwd/metric ton	Soluble Loss - Percent of Total		
		U	Pu	Cs γ
IV-4-S	9,000	1.01	1.06	28.2
IV-3-P	10,900	0.21	0.54	11.4
X-1-S	36,300	1.18	1.86	47.2
VII-3-P	38,900	4.32	0.78	51.5
V-4-S	42,700	0.61	0.67	73.1
IX-1-P	47,600	0.41	1.28	47.7
VII-2-P	49,900	0.57	0.53	46.4
V-3-P	54,400	1.36	2.35	62.0
VI-1-S	69,100	1.79	1.68	93.7
VII-1-S	70,300	0.59	0.20	45.8
V-2-P	77,400	3.09	4.50	68.0
Average		1.55	1.54	59.5

4.4.2 Fission-Product Solubility

Chemical analysis of the product solution from leaching the 99,000-Mwd/metric ton specimen for 3 hr in 5 M HNO_3 showed uranium and plutonium concentrations of 125 and 29 mg/ml, respectively. The spectrographic analysis of the solution is given in Table 3. About 3.33 mg of fission product elements per ml were found by this method; adding 0.272 mg/ml ^{137}Cs (calculated from ^{137}Cs and its specific activity), a total of 3.60 mg of fission products per ml was found. Assuming 0.75 g of solid fission products and 0.25 g of fission gases are formed per gram fissioned, and a 6% yield of ^{137}Cs, the total concentration of fission products in solution should be about 0.272/0.06 x 0.75, or 3.20 mg/ml. This value is in reasonable agreement with the results of the spectrographic analysis.

Table 3. Concentrations of Fission Products in Nitric Acid Leach Solutions from 99,000-Mwd/metric ton Specimen

Determined Spectrographically

Element	Range (mg/liter)	Average (mg/ml)
Ag	4.3	--
Ce	750-1500	1.125
Cr	4.6	--
Cu	3.7	--
Fe	127	--
La	400-800	0.600
Mn	2.1	--
Mo	600	0.600
Nd	400-800	0.600
Ni	24	--
Pd	20-50	0.035
Pr	100-500	0.300
Ru	20-50	0.035
Y	10-50	0.030
Zr	6.4	0.006
	Total	3.331

4.4.3 Insoluble Residues

Spectrographic and chemical analyses of the insoluble residue from the 3-hr leach of fuel (irradiated to 99,000 Mwd/metric ton) in 5 M HNO_3 showed that it contained 1.5 mg of U, 2.0 mg of Pu, 28 mg of Mo, 24 mg of Zr, 1 mg of Pd, and 3 mg of Rh, totalling 59 mg, or 2.2% of the fuel oxide weight. The uranium and plutonium content of the residue was 0.13% of the total. Gamma-ray scanning showed that nearly all the radioactivity was due to ^{106}Ru.

Capsule VII-1-S (70,300 Mwd/metric ton) was nearly completely declad in 3.5 hr in boiling 6 M H_2SO_4, and the core dissolved for 1 hr in 10 M HNO_3.

The residue from the core and cladding weighed 226 mg or about 8% of the weight of the UO_2-PuO_2, and 3.7% of the total specimen weight. It contained 0.8 mg of U + Pu (0.03% of the total) plus 120 mg of Fe, 54 mg of Cr, 17 mg of Ni, 3 mg of Mn, 2 mg of Mo, 1 mg of Cu, and 0.5 mg of Al, totalling 198 mg of metals (not oxides). The gamma activity of the residue was due to ruthenium and cesium.

Capsule VI-1-S (69,100 Mwd/metric ton) was also declad for 3.5 hr, and the core dissolved in 7 M HNO_3 for 1 hr. The residue weighed about 60 mg (0.9% of the total specimen weight and 2.4% of the core weight). It contained 3.4 mg of U + Pu (0.15% of the total), 1 mg each of Fe, Cr, Ni, about 3 mg Mo, 0.2 mg of Zr, and traces of other elements.

In general, it appears that the insoluble residues from the leaching of UO_2-PuO_2 (Fig. 6a) consist of small amounts of undissolved oxide and "dead" fission-product Mo, Zr, Pd, and Rh, along with some Ru gamma activity. The heavier residues from declad UO_2-PuO_2 (Fig. 6b) are principally insoluble cladding and "stainless-steel" oxides plus undissolved core and inactive fission products. It thus appears that some form of feed clarification is required before solvent extraction or ion exchange is applied to recover the uranium and plutonium.

4.4.4 Change in Isotopic Composition of Fuel as a Function of Irradiation

The isotopic composition of the uranium in the fuel before irradiation was 46.2% ^{235}U and 53.3% ^{238}U; that of the plutonium was 94.2% ^{239}Pu and 5.8% ^{240}Pu. The overall composition of the unirradiated mixed oxides was 18.81% ^{239}Pu, 1.20% ^{240}Pu, 37.86% ^{235}U, and 42.13% ^{238}U.[1,2] Figure 7 shows the small change in isotopic composition of the uranium and plutonium as a function of irradiation level and indicates that GE-VAL successfully obtained the desired high burnups while maintaining a relatively constant Pu:U ratio through enrichment of the uranium to about 50% ^{235}U. Growth of the heavier plutonium isotopes is clearly shown in Fig. 7.

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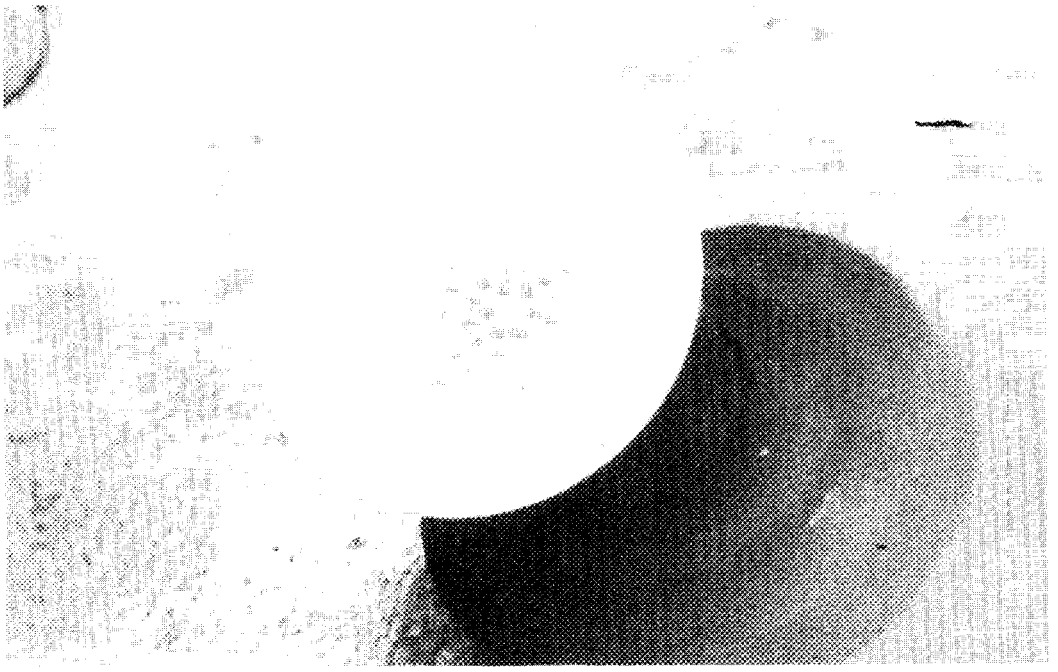

(a)

PHOTO 80407

(b)

Fig. 6. (a) Residue from Leaching Irradiated UO_2-PuO_2. (b) Chemically Declad UO_2-PuO_2, Showing Excessive Amount of Undissolved Cladding.

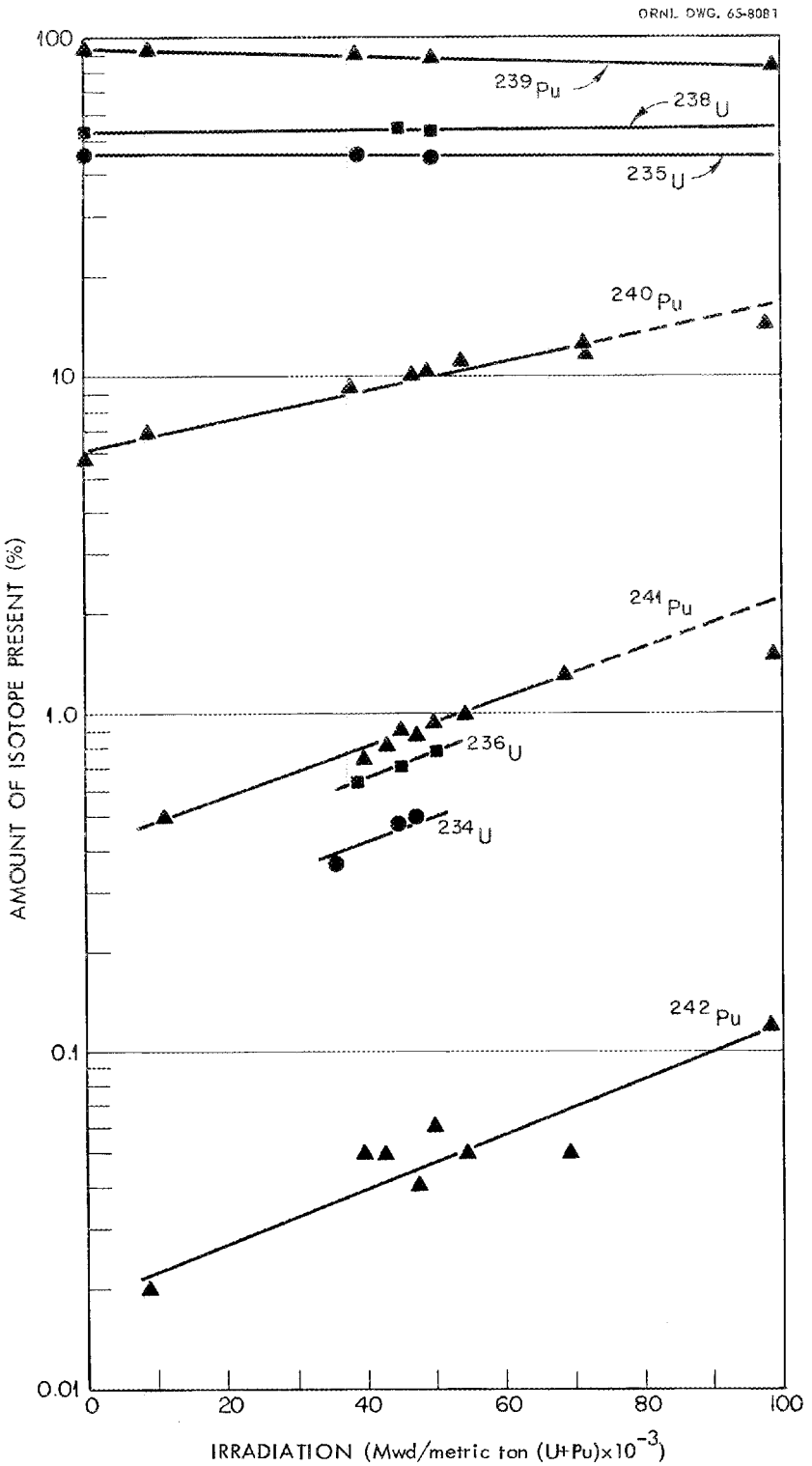

Fig. 7. Change in Isotopic Compositions of Uranium and Plutonium as a Function of Irradiation Level.

5. DISCUSSION AND CONCLUSIONS

5.1 Decladding Losses

Chemical decladding (with 6 M H_2SO_4) of this type of fuel does not appear economically feasible because the losses of uranium and plutonium to the decladding solution were rather high, i.e., ~1.5%. The requirement of additional processing steps to recover the fuel from the Sulfex decladding solutions would be economically impractical.

In addition to the high uranium and plutonium losses to the decladding solution, the presence of about 60% of the cesium in the solution would cause problems in waste management. For example, in earlier work with stainless-steel-clad UO_2 and ThO_2-UO_2,[10,11] relatively small amounts of cesium were found in the decladding solutions — 1 to 2% from UO_2, and about 3 to 4% from sol-gel ThO_2-UO_2 irradiated up to 25,000 Mwd/metric ton. Hence, the design and cooling of waste storage tanks could be based mainly on the presence of ^{60}Co. The additional heat from cesium would require the use of more dilute solutions and larger waste tanks.

Irradiation conditions were responsible for the increase in the amount of cesium found in the decladding solutions from these Fast Breeder capsules over that found in earlier studies. The NaK-cooled Fast Breeder capsules were irradiated at high temperature, that is, up to 1260°F at the cladding surface, versus cladding temperatures of less than 212°F for the water-cooled UO_2 and ThO_2-UO_2 prototypes. Rider and Ruiz[12] attribute the presence of the cesium to the radial migration of ^{137}Xe from the core to cooler cladding surfaces and subsequent decay to ^{137}Cs. Slosek and Weidenbaum found all the ^{137}Cs from vibratory-compacted UO_2 on the cladding walls during tests under high-performance conditions.[9] Rider also noted cesium oxide dissociates at 360 to 400°C, giving cesium metal and oxygen. Since the center temperature of the fuels may be in excess of 2000°C, the cesium would be present as a gas, and condense on the cooler cladding. Davies *et al.*,[13] used postirradiation heating to measure the rate of emission of volatile fission products from UO_2. They found that at temperatures less than 1600°C the diffusion rates of I, Te, and Cs were the same as the rate for Xe in low-density UO_2 and exceeded the rate

for Xe in high-density specimens. At greater than 2000°C, the emission of volatile fission products approached 100%. They attributed the diffusion to the sweeping out of fission products by the moving grain boundaries in the UO_2 during grain growth. Gerhart's postirradiation examination of the Fast Breeder capsules, which showed grain growth from the central void toward the fuel periphery as well as fission-gas bubbles within the fuel grains, support this hypothesis.

5.2 Dissolution Rates

The experiments on irradiated fuel specimens confirmed previous results with unirradiated oxides: that solid solutions of UO_2-PuO_2 are soluble in nitric acid at concentrations higher than 3 M. It is also known from previous work that fluoride is required in addition to nitric acid when dissolving PuO_2. This illustrates a problem in fuel processing. If great care is not used in fuel fabrication to ensure the formation of a solid solution of UO_2-PuO_2, the processor may be unable to dissolve the fuel in a tank designed for use with pure nitric acid rather than the more corrosive HNO_3-HF mixture. Uriarte and Rainey[1] showed that aluminum cannot be added to complex the fluoride, and thus reduce corrosion, since the aluminum fluoride complex is so strong that the fluoride ion is not available to accelerate the reaction between PuO_2 and nitric acid.

5.3 Fission Product Solubility and Dissolution Residues

The fission products from UO_2-PuO_2 irradiated to 99,000 Mwd/metric ton were soluble in a 5 M HNO_3--0.53 M $UO_2(NO_3)_2$--0.12 M $Pu(NO_3)_4$ solution, with the exception of small amounts of Mo, Zr, Pd, and Rh. This insoluble residue may amount to 2 or 3% of the weight of the core and must be removed from the fuel solution before reprocessing by solvent extraction or ion exchange.

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