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PROCESSES FOR RECOVERY OF URANIUM AND
THORIUM FROM GRAPHITE-BASE FUEL
ELEMENTS. PART II

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OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

PROCESSES FOR RECOVERY OF URANIUM AND THORIUM
FROM GRAPHITE-BASE FUEL ELEMENTS.

PART II

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ABSTRACT

Laboratory-scale tests on methods for recovering uranium and thorium from graphite-base reactor fuel elements are reported. The 90% HNO_3 process, which involves simultaneous disintegration and leaching in 21 M HNO_3 , is applicable to all fuel elements which do not contain coated fuel particles. Leaching of irradiated (0.001% burnup) fuels containing 3 and 12% uranium recovered ~99.3 and 99.9%, respectively, of the uranium in two 4-hr leaches with boiling acid. The graphite residue retained >50% of the long-lived fission products. Three successive leaches of fuel containing uranium and thorium recovered ~99% of both elements. Uranium recoveries by combustion in oxygen followed by dissolution of the ash in nitric acid or fluoride-catalyzed nitric acid are quantitative only when the fuel is not coated, does not contain Al_2O_3 -coated fuel particles, and is free from impurities such as iron. During combustion up to 95% of the Ru-106 was volatilized from irradiated specimens. Recoveries, by leaching with 70% HNO_3 , from fuel specimens containing Al_2O_3 -coated fuel particles were greater than 99% when the specimens were ground finer than 200 mesh to ensure crushing of the fuel particles.

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1.0 INTRODUCTION

A systematic evaluation of potential methods for processing graphite-base fuel elements has been undertaken at ORNL, development of such methods being spurred by the recent interest in gas-cooled reactors in the U. S. Differences in the several power reactor concepts that have been proposed (1), such as type of coolant, coolant temperature, and rate of fission gas release, are reflected in the variety of fuel element types being studied. These can be divided into at least three categories: (1) those which have no coating and do not contain coated fuel particles; (2) those which are coated with a material such as graphite, pyrolytic carbon, or SiC; and (3) those which contain fuel particles coated with pyrolytic carbon, Al_2O_3 , or BeO before being dispersed in the matrix.

Techniques currently being studied at ORNL for head-end processing, prior to solvent extraction, are disintegration and leaching with 90% HNO_3 , combustion followed by dissolution of the ash, and grinding and leaching of the fuel. Data on 90% HNO_3 leaching plus the effects of nitric acid concentration, uranium content of the fuel, and leaching temperature, are given together with preliminary combustion-dissolution data, a few further grind-leach data, and data on the applicability of these processes to several types of fuel. The literature on the reaction of graphite with nitric acid and on combustion of graphite is surveyed.

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Potential Processes. Processing methods that have received more than cursory attention include grind-leach techniques (2-6), simultaneous disintegration and leaching with 90% HNO_3 (7), combustion in air or oxygen (6), and electrolytic disintegration (4,6,8). Disintegration of fuels with bromine (6,7) or interhalogens (7) prior to acid leaching has also been studied, and the influence of ultrasonic energy on the leaching of urania-impregnated fuel specimens has been investigated (9). Work at BNL indicated that graphite-base

fuels disintegrate in NO_2 -HF solutions at 160 to 200°C (10). Electrolytic disintegration of fuel specimens was used at Battelle Memorial Institute to separate coated fuel particles from the graphite matrix (11).

In the 90% HNO_3 process recoveries from uncoated uranium-bearing fuels are usually >99% from fuels containing greater than ~2% uranium but decrease to ~96% for 0.7% uranium fuel. Recoveries from fuel containing both uranium and thorium are high in three or four successive leaches. Recoveries are equally high from graphitized (fired above 2400°C) or ungraphitized (baked below 1000°C) fuels although graphitized fuels are disintegrated more readily with 90% HNO_3 . Fuel elements containing coated fuel particles cannot be processed, although those elements which are coated but do not contain coated fuel particles probably could be processed after rough crushing to destroy the integrity of the coating. Unfueled graphite claddings are only slowly disintegrated.

The combustion-dissolution process is applicable to all types of graphite-base fuels except those containing Al_2O_3 -, and, probably, BeO -coated fuel particles. Rough crushing of fuels coated with SiC or similar materials probably would be required before combustion. Uranium and/or thorium recoveries are virtually quantitative from uncoated fuel elements. If a SiC coating is present, some uranium is lost to the siliceous residue. Up to 95% of the Ru-106 may volatilize during combustion.

The grind-leach process is applicable to all types of fuels proposed, but losses of uranium and/or thorium to the graphite residue are generally higher than desired, particularly from fuels containing <5% uranium and from coated fuels. However, this method may be the only one which allows recovery of fissile and fertile material from elements containing coated fuel particles. Grinding to about 200 mesh is required in the latter case to ensure rupture of the coatings.

Future Work. Development of processing methods for graphite-base fuels is in the embryonic stage. In order to determine the feasibility of the various potential processes, extensive engineering study in addition to more laboratory investigation is required. Initial emphasis in the laboratory studies should perhaps be placed on determining the safety of the 90% HNO_3 process. Under flowsheet conditions, the graphite is slightly attacked by 90% HNO_3 as evidenced

by the colored solutions produced. A thorough investigation of the reactions between fueled and unfueled graphite with nitric acid has been started with special attention being given to the off-gas composition and to the identification of dissolved organic species. A separate program, in which the reactions of pure uranium and thorium carbides with aqueous reagents such as nitric acid are being studied, has been in existence for about two years. In addition, preliminary solvent extraction experiments have been performed. Ultimately, a thorough evaluation of feed adjustment and solvent extraction methods for the various head-end techniques will be required. Corrosion, particularly in the 90% HNO_3 and combustion-dissolution processes, may be a limiting factor; therefore an intensive effort to find suitable materials of construction is planned. The laboratory studies will ultimately culminate in hot-cell experiments with fully irradiated fuel specimens.

2.0 PROCESS WITH 90% HNO_3

A tentative batch flowsheet developed on a laboratory scale for uncoated graphitized fuels has been reported (7). These fuels swell and then disintegrate in 90% (21.2 M) HNO_3 at either room temperature (Fig. 1) or the boiling point. Particle size reduction is rapid during the first few hours. Leaching, which takes place simultaneously, is more efficient at the boiling point than at room temperature. The leach liquor, which is highly colored due to reaction of the graphite and/or uranium carbide with the acid, is removed from the graphite residue powder by vacuum filtration, and the residue is washed three times with water, the wash liquid being removed by vacuum filtration each time. The fuel is then leached again for 4 hr and washed. The leach liquors, which are ~20 M in HNO_3 , can be evaporated to recover 21 M HNO_3 for recycle or combined with the wash solutions for buildown prior to solvent extraction.

2.1 Recoveries from Various Types of Fuel

2.1.1 Uncoated Uranium-bearing Fuel

Effect of Uranium Content. Prior studies (7) with uncoated fuel specimens indicated that uranium recovery increases as the uranium content of the fuel increases. In two 4-hr leaches with boiling 90% HNO_3 , recoveries were >96%

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Fig. 1. Disintegration of graphite--15% UO_2 fuel specimen in 90% HNO_3 in 1 hr contact at 25°C .

from fuel containing $\sim 0.7\%$ uranium, at least 99.5% from fuel containing 2.5% uranium, and $>99.8\%$ from fuel containing $>5\%$ uranium. These results were confirmed in further studies with specimens from the same batches. Uranium was almost totally recovered in the first 5 hr of a 48-hr leach (3.5 ml of acid per gram of fuel) from fuels containing $>2.5\%$ uranium but was leached at a much lower rate from a specimen containing 0.7% uranium (Table 1, Fig. 2).

Effect of Multiple Digestions. In all cases uranium recoveries were higher in two 4-hr leaches than in a single 48-hr digestion. For example, with fuel containing 12.9% uranium, the uranium loss to the residue was only 0.06% after two 4-hr leaches but was 0.4% after a single 48-hr leach.

In a series of experiments at 60°C with 25-g samples containing $\sim 3\%$ UO_2 , multiple leaching with or without water washing of the residue between leachings not only produced greater disintegration of the fuel specimens,

Fig. 2. Effect of uranium content of fuel on recovery of uranium from graphite- UO_2 fuel specimens by leaching with boiling 90% HNO_3 .

Table 1. Recovery of Uranium from Graphite- UO_2 Fuel Specimens
by Leaching with Boiling 90% HNO_3

Volume of reagent: 3.5 ml of acid per gram of specimen

U in Specimen, %	Leaching Time, hr	U Loss to Residue, %	U in Specimen, %	Leaching Time, hr	U Loss to Residue, %
0.695	1	26.4	7.94	1	2.3
	2	18.0		6	2.2
	3	16.4		24	0.49
	4	13.9	12.9	1	2.1
	6	13.2		6	0.54
	24	8.5		24	0.36
	48	3.2		48	0.38
2.56	2	5.7			
	4	4.2			
	6	2.8			
	24	0.85			
	48	0.69			

but also resulted in higher uranium recoveries (Table 2). The geometric mean particle size of the residue from a single 8-hr leach was ~1100 μ , while the mean sizes of the residues from two series of four 2-hr leaches, with water washings between leachings in one series and not in the other, were 500 and 1000 μ , respectively. With the single 8-hr leach, the uranium loss to the residue was 3.5%, while losses in the experiments with multiple leachings were 0.1%. The only advantage gained by water washing after each leach was the higher uranium recovery over the first two leaches. After four leaches, however, recoveries were essentially the same whether the residues were washed or not. The results suggest that countercurrent extraction with 90% HNO_3 at low temperature might be an easy method for processing this type of fuel. Experimental conditions were chosen so that acid concentrations would be about the same during each leach.

Table 2. Leaching of Unirradiated Graphite—3% UO_2 Fuel
Specimens at 60°C with 90% HNO_3

Experiment A: specimen leached once with 90% HNO_3 (3.5 ml per gram of specimen) for 8 hr and residue thoroughly washed with water
Experiment B: specimen subjected to four 2-hr leaches with 90% HNO_3 ; each leach followed by thorough washing and drying of residue.
Experiment C: specimen subjected to four 2-hr leaches with 90% HNO_3 ; residue dried but not washed after each of first three leaches and washed after final leach.

Expt.	Leach	Final H^+ Conc in Leach Soln, M	Amount of Uranium, %		Geometric Mean Particle Size of Residue, μ
			In Leach	Lost to Residue	
A	1	20.9	96.47 ^a	3.53	1100
B	1	20.7	95.9 ^a		
	2	20.9	3.68 ^a		
	3	20.8	0.21 ^a		
	4	20.4	0.12 ^a	0.075	500
C	1	20.6	82.0		
	2	20.7	14.1		
	3	20.7	2.95		
	4	20.7	0.78 ^a	0.099	1000

^aIncludes uranium extracted in wash following leach.

With either single or multiple leachings, uranium was easily recovered from TURRET fuel specimens (~7% uranium), type AUC graphite impregnated with uranyl nitrate solution and baked (12). Recoveries were >99.9% after two 4-hr leaches at either 25°C or the boiling point (Table 3). The uranium was also recovered by extended leaching with boiling acid with a loss of only 0.14% after 24 hr.

Table 3. Recovery of Uranium from TURRET Fuel Specimens

Uranium in Sample, %	Leaching Conditions			Uranium Recovered, %		
	No. of Leaches	Total Time, hr	Temp, °C	1st Leach and Wash	2nd Leach and Wash	Residue
7.86	2	8	25	96.2	3.70	0.094
7.11	2	8	93	99.3	0.68	0.012
6.57	1	24	93	99.9	-	0.14

Effect of Particle Size. With specimens containing the same percentages of uranium, losses to the powdered residues decreased somewhat with decreasing particle size, but losses were not the same for specimens of the same particle size but different initial uranium concentrations (Fig. 3). The data indicate that >99% of the uranium from specimens containing 0.7-15% uranium is recovered when the mean particle size is reduced to about 80 μ . The slight dependence of loss on mean particle size for specimens containing >2.5% uranium confirms previously obtained grind-leach data (2).

Use of Product Solution as Leachant. The amounts of uranium recovered from fuel specimens containing 7.68% uranium by leaching at 25°C with the product solution from a prior leach were essentially the same as in leaching with fresh nitric acid:

	Uranium Recovered, %		
	1st Leach and Wash	2nd Leach and Wash	Residue
90% HNO_3 (21.5 M)	97.6	2.2	0.19
21 M HNO_3 —0.09 M $\text{UO}_2(\text{NO}_3)_2$	97.9	1.9	0.14

Fig. 3. Effect of mean particle size on uranium loss in leaching of graphite-UO₂ fuel specimens with boiling 90% HNO₃.

Experiments with Irradiated Fuel. A series of runs was made with 90% HNO₃ and irradiated (0.001% burnup) specimens containing 3 to 15% uranium, presumably as the dicarbide. Uranium recoveries, as expected from prior work (7) were dependent on the uranium concentration in the specimen, the leaching temperature, and the reaction time. With fuel containing ~3% uranium, losses to the graphite residue after two 4-hr leaches with 90% HNO₃ and water washing were ~1.2 and 0.65% when the reaction temperatures were 25 and 93°C, respectively (Table 4). The loss was only 0.15% in two 24-hr leaches with boiling acid. With specimens containing 12-15% uranium, losses after two 4-hr leaches were ~0.1 and 0.03% in leaches at 25 and 93°C, respectively (Table 4). In contrast to the results with 3% fuel, the loss was not decreased further by leaching the specimens twice for 24 hr with boiling 90% HNO₃.

Generally, 60-70% of both the uranium (Table 4) and nitric acid were recovered in the first leach filtrate, and 20-30% of the original amount of both in the first water wash (Table 5). These data indicate that the retention was due strictly to sorption of the leach solution, with no selective sorption of uranium or nitric acid.

Table 4. Uranium Recovered by 90% HNO₃ Leaching of Uncoated Irradiated Graphite-base Fuel Specimens

Fuel specimen burnup: 0.001%

Run No.	U in Sample, %	Leaching Conditions ^a		Uranium Recovered, %				
		Time, hr	Temp, °C	1st Leach	1st Leach and Washes	2nd Leach	2nd Leach and Washes	Residue
A-1	3.00	4	25	-	95.4	-	3.5	1.1
A-3	2.81	4	25	60.1	95.1	2.6	3.6	1.3
A-2	3.02	4	93 ^b	64.9	97.3	1.1	2.0	0.62
A-4	2.82	4	93	70.0	96.7	2.0	2.6	0.66
A-5	2.88	24	93	70.5	99.3	0.36	0.51	0.15
B-1	12.2	4	25	-	98.5	-	1.4	0.11
B-2	13.7	4	25	69.8	98.4	1.2	1.6	0.07
B-5	11.7	4	25	74.9	97.8	1.4	1.9	0.17
B-3	15.2	4	93	54.2	99.3	0.44	0.63	0.03
B-4	11.8	4	93	66.8	99.1	0.63	0.84	0.02
B-6	11.7	24	93	63.2	99.3	0.52	0.76	0.02
B-7	12.0	24	93	70.4	99.1	0.58	0.80	0.02

^aSpecimens subjected to two leaches, each for the time shown.

^bThe approximate boiling point of 90% HNO₃.

Table 5. Uranium Recovered in First Wash of Residue from 90% HNO₃ Leaching of Uranium-Graphite Fuel Specimens

Conditions given in Table 4

Run No.	Amount Recovered in 1st Wash, % of original	
	Uranium	Nitric Acid
A-1	-	-
A-3	30.8	23.6
A-2	22.5	24.9
A-4	23.9	23.0
A-5	26.6	25.7
B-1	-	-
B-2	27.5	23.5
B-5	21.8	18.8
B-3	41.4	27.5
B-4	28.6	29.6
B-6	34.4	35.2
B-7	25.2	26.5

2.1.2 Uncoated Thorium-bearing Fuel

At least 99.7% of both the uranium and thorium were recovered from thorium-bearing fuel samples in three leaches with boiling 90% HNO_3 (Table 6). Two types of thorium-bearing fuel samples were used: HTGR-1, containing ~1.5% uranium and 7.2% thorium as oxide particles dispersed homogeneously throughout the graphite matrix, and HTGR-2, containing an average of ~1.2% uranium and 15% thorium as uncoated, coprecipitated 150- μ dicarbide particles. The HTGR-2 sample was taken from an HTGR (13) prototype compact (2.25 in. dia) comprised of a solid graphite core surrounded by a 3/8-in. annular region containing 30 wt % dicarbide particles.

Thorium recoveries were high only after three leaches, particularly with sample HTGR-1. The presence of 0.05 M HF in the nitric acid had no beneficial effect on the recovery of thorium from sample HTGR-1. The leaching temperature was very important. With sample HTGR-2, uranium and thorium losses to the graphite residue decreased from ~10 to 0.2% when the leaching temperature was increased from 25°C to the boiling point, ~93°C (Table 6).

Table 6. Recovery of Uranium and Thorium from Uncoated Graphite-base Fuels by 90% HNO_3

Each leach for 4 hr with boiling acid

Sample, HTGR-	Fuel Comp, %		Amount Recovered, %							
			1st Leach and Wash		2nd Leach and Wash		3rd Leach and Wash		Residue	
	U	Th	U	Th	U	Th	U	Th	U	Th
1	1.5	7.2	96.4	85.5	2.6	7.7	-	-	1.1	6.8
1	1.45	6.95	98.6	86.2	1.37	11.8	-	-	0.24	1.93
1 ^a	1.47	7.14	97.6	87.2	2.37	7.98	-	-	0.16	4.81
1	1.50	7.21	97.7	85.5	2.31	13.0	0.10	1.17	0.06	0.25
2 ^b	1.18	14.3	80.7	83.7	8.0	5.8	-	-	11.4	10.4
2	1.28	15.0	95.3	99.0	4.58	0.88	-	-	0.10	0.16

^aLeachant contained 0.05 M HF.

^bLeaching conducted at 25°C.

2.1.3 Fuels Containing Al_2O_3 - or Carbon-coated Fuel Particles

Results of preliminary experiments on leaching Al_2O_3 - or pyrolytic carbon-coated fuel particles with 90% HNO_3 were discouraging. Under flowsheet conditions (7), <10% of the uranium was recovered from the specimens studied.

Two types of specimens were available for study: HTGR-3, from the annular region of a prototype HTGR fuel compact containing 9.74% uranium and 33.5% thorium as pyrolytic carbon-coated 250- μ UC_2 - ThC_2 particles dispersed in a graphite matrix, and FA-22, a Pebble Bed Reactor (14) prototype sphere containing ~8% uranium as 125- μ Al_2O_3 -coated UO_2 particles dispersed in an ungraphitized matrix. The Al_2O_3 coating was 17 μ thick; the $\text{UO}_2/\text{Al}_2\text{O}_3$ weight ratio was 2.7. Recoveries by leaching the specimens twice with boiling 90% HNO_3 under flowsheet conditions (7) were

	<u>U, %</u>	<u>Th, %</u>
HTGR-3	6.9	4.9
HTGR-3	6.0	4.3
FA-22	0.8	-

Some of the particles were fractured when the samples were cut, and recoveries would probably be lower with integral fuel specimens.

2.1.4 SiC-coated Fuels

A fractured SiC-coated Pebble Bed Reactor (14) specimen (FA-6) was leached twice with 90% HNO_3 under the usual conditions. While no disintegration of the ungraphitized matrix was apparent, 98.5% of the uranium was recovered. The SiC coating did not appear to be affected by the nitric acid, so that at least rough crushing of fuel elements of this type would be required prior to the leaching step.

2.2 Fission Product Behavior

Experiments with irradiated (~0.001% burnup) fuel specimens containing 3-15% uncoated uranium dicarbide particles dispersed homogeneously throughout the graphitized matrix were made for preliminary evaluation of waste disposal problems. The long-lived fission products, viz., Zr-95, Ru-106, Cs-137, and Ce-144, were leached from the graphite matrix less rapidly than the uranium, the leaching rate being different for each nuclide. For example, in two 4-hr leaches with boiling 90% HNO_3 , 54, 66, 80, and 44%, respectively, of the

Zr-95, Ru-106, Cs-137, and Ce-144 were leached (Table 7). These data agree qualitatively with those reported elsewhere (6). Uranium recoveries were nearly quantitative (Sect. 2.2.1). The data indicate that the amounts of fission products leached from specimens containing 12-15% uranium were slightly higher than those from specimens containing ~3% uranium.

The increase in fission product leaching was pronounced when the samples were leached twice for 24 hr instead of the usual 4 hr (runs B-6 and 7). Since the fuel specimens were only slightly irradiated and long-decayed (~1.5 years) and were not necessarily representative of fuels proposed for power reactors such as the HTGR (13) and PBR (14, 15), more extensive experiments with highly irradiated specimens will be needed to verify these preliminary results.

In several experiments with boiling 90% HNO_3 , no evidence could be found of volatilization of Ru-106, contrary to results reported from Harwell (6) for dilute nitric acid.

2.3 Particle Size of Residues

Particle size data are useful in determining the optimum conditions for washing the powders and for forming slurries that will be jetted to waste. The effects on particle size distribution of nitric acid concentration, uranium content of the fuel, and digestion time were therefore investigated briefly.

Effect of Nitric Acid Concentration. Experiments with unirradiated, uncoated specimens containing about 8% UO_2 showed that the concentration of the boiling nitric acid must be $>20 \text{ M}$ to effect disintegration (Fig. 4a). However, the mean particle size decreased only from about 250 to 100 μ when the nitric acid concentration was increased from 21 to 23.9 M . From the viewpoints of effectiveness, safety, and availability, 90% HNO_3 (21.2-21.7 M) appears to be the optimum concentration.

Effect of Uranium Content and Time. Pure graphite disintegrated very slowly in boiling 21.6 M HNO_3 , the mean particle size being only ~550 μ after a 48-hr digestion with boiling 90% HNO_3 (Fig. 4b). In contrast, an unirradiated specimen containing 0.7% uranium was reduced to a powder with a mean particle size of ~200 μ in 5 hr reflux.

Fig. 4. Effect on mean particle size of residue from leaching of graphite UO_2 fuel specimens with boiling nitric acid of (a) nitric acid concentration with $\sim 8\%$ UO_2 specimens and (b) uranium content and time with 90% HNO_3 .

Table 7. Distribution of Fission Products in Two-leach 90% HNO₃
Experiments with Irradiated Graphite-UC₂ Fuel Specimens

Leaching conditions given in Table 4

Run No.	Amount of FP in Sample, %								Residue
	1st Leach	1st Wash	2nd Wash	3rd Wash	2nd Leach	1st Wash	2nd Wash	3rd Wash	
Zr-95									
A-1	41.6 ^a	-	0.51	-	19.1 ^a	-	0.59	0.087	38.2
A-3	7.71	4.54	0.19	0.01	4.50	1.03	0.05	0.007	81.9
A-2	30.8	14.2	3.8	0.43	6.0	4.3	0.32	0.026	40.0
A-4	28.0	9.4	0.30	0.08	6.7	1.2	0.08	0.03	54.2
A-5	46.6	20.2	1.06	0.078	8.24	2.82	0.33	0.06	20.5
B-1	7.85 ^a	-	0.30	-	45.3 ^a	-	0.27	0.048	46.2
B-2	No analyses	-	-	-	-	-	-	-	-
B-5	10.6	3.80	0.29	0.02	3.51	1.90	0.24	0.03	79.6
B-3	17.5	7.6	1.4	0.24	10.6	2.8	0.37	0.09	59.5
B-4	39.1	19.4	2.53	0.40	0.28	7.49	0.82	0.25	29.7
B-6	26.9	17.2	0.87	0.07	14.9	5.5	0.62	0.08	33.8
B-7	32.0	11.5	1.2	0.05	17.6	5.4	0.31	-	31.8
Ru-106									
A-1	36.2 ^a	-	2.48	0.93	13.5 ^a	-	0.54	-	46.3
A-3	18.4	18.7	2.13	0.86	14.7	3.68	0.27	0.10	41.2
A-2	38.6	12.3	3.65	0.56	4.62	3.97	0.21	0.05	36.0
A-4	38.1	12.4	0.69	0.01	4.4	0.69	0.01	0.01	43.6
A-5	38.5	12.4	0.95	0.03	24.6	0.68	0.10	0.02	22.7
B-1	24.0 ^a	-	0.45	0.042	12.3 ^a	-	-	-	63.2
B-5	18.0	7.90	0.62	-	11.7	3.97	0.24	0.04	57.5
B-3	35.8	11.3	2.1	0.11	11.9	2.0	0.08	0.02	36.7
B-4	46.6	16.8	1.64	0.12	13.5	2.0	0.12	0.01	19.2
B-6	34.4	19.7	0.83	-	12.4	4.9	0.44	-	27.3
B-7	43.2	13.3	1.92	-	14.6	4.73	-	-	22.2

Table 7. (Cont.)

Run No.	Amount of FP in Sample, %								Residue
	1st Leach	1st Wash	2nd Wash	3rd Wash	2nd Leach	1st Wash	2nd Wash	3rd Wash	
Cs-137									
A-1	14.6 ^a	-	2.11	0.46	1.84 ^a	-	0.20	0.13	80.7
A-3	75.4	8.73	2.64	1.84	1.99	1.02	0.25	0.07	8.11
A-2	37.1	16.6	5.1	1.49	5.44	2.27	0.44	0.15	31.4
A-4	49.4	17.0	1.8	0.75	7.2	1.3	0.01	0.006	22.4
A-5	65.0	18.7	1.60	0.11	1.34	0.14	0.03	-	13.0
B-1	49.7 ^a	-	7.80	1.09	12.3 ^a	-	0.81	0.26	28.0
B-5	25.5	14.2	6.69	1.14	9.18	4.09	0.96	0.28	38.0
B-3	47.6	18.2	3.2	0.53	8.9	0.24	0.13	0.03	21.1
B-4	56.8	22.3	2.89	0.31	8.66	1.82	0.15	0.01	7.12
B-6	52.8	27.1	1.5	0.26	8.8	2.3	0.28	0.02	6.9
B-7	58.2	18.6	2.79	0.32	9.0	2.47	0.15	0.02	8.51
Ce-144									
A-1	18.8 ^a	-	1.80	0.25	3.24 ^a	-	0.18	-	75.7
A-3	10.1	11.1	0.89	1.43	3.58	3.71	0.08	0.001	69.1
A-2	8.76	7.50	2.56	0.86	4.54	12.5	1.15	0.003	62.1
A-4	10.6	9.8	0.54	0.03	11.8	11.4	0.54	0.06	55.3
A-5	44.4	21.2	1.23	0.003	3.50	2.74	0.13	-	26.8
B-1	21.5 ^a	-	1.42	0.17	2.47 ^a	-	0.041	-	74.4
B-5	14.6	5.60	0.40	-	1.66	1.67	0.10	0.002	75.9
B-3	19.3	9.6	1.7	0.06	0.70	7.0	0.31	0.003	61.3
B-4	23.4	12.4	1.56	0.02	7.35	10.9	0.75	0.002	43.6
B-6	27.0	19.8	0.65	0.02	22.3	11.5	0.84	0.008	17.9
B-7	25.7	10.9	15.6	0.013	8.60	11.9	0.64	0.02	26.6

^aIncludes first wash.

Unirradiated specimens containing 2.5-13% uranium were disintegrated to finer particles than the specimens containing only 0.7% uranium. After 10 hr of reflux, for example, the mean sizes were ~110 and 170 μ for specimens containing 2.5-13 and 0.7% uranium. The extent of disintegration of fueled graphite was not greatly affected by the uranium content in the range 2.5-13% uranium.

Effect of Temperature. With 90% HNO_3 acting on irradiated graphite- UC_2 fuel containing 3-15% uranium, the apparent geometric mean Stokes diameter of the residual powder varied with reaction temperature and time. In two 4-hr leaches, the mean diameter decreased from 300-400 to 200-300 μ when the reaction temperature was increased from 25°C to the boiling point, ~93°C (Table 8). In two 24-hr leaches with boiling acid the mean diameter was decreased to 100-200 μ .

Table 8. Particle Sizes in Residues from 90% HNO_3 Leaching of Irradiated Graphite- UC_2 Fuel Specimens

Each specimen leached twice for the time indicated

Uranium in Sample, %	Leaching Conditions		Geom. Mean Stokes Dia, μ	Geom. Stand. Deviation
	Time, hr	Temp, °C		
2.81	4	25	295	1.83
11.7	4	25	390	2.11
12.2	4	25	390	2.11
2.82	4	93	208	1.71
3.02	4	93	295	1.74
11.8	4	93	213	1.90
15.2	4	93	259	1.99
2.88	24	93	112	1.24
11.7	24	93	149	1.62
12.0	24	93	187	1.62

Techniques for Determining Particle Sizes. Two techniques for determining particle size were used. In the experiments with unirradiated specimens the residual powders were washed with water after the nitric acid digestion, air-dried, weighed, and sieved. Each sieve fraction was subsequently weighed. For purposes of correlation, it was assumed that the particles were spherical and that all those with diameters greater than the sieve opening were caught on that sieve. These assumptions are not necessarily valid (16, 17), and generally only one experiment was made under each set of conditions.

In the experiments with irradiated fuel specimens, particle size distribution of the powders was determined by a sedimentation method (18), assuming the density of the particles to be 1.7 g/cc. The data from both series of experiments were best correlated by log-probability plots (Fig. 5). The mean (50%) size obtained from such plots is the geometric mean (16, 17); the geometric standard deviation, σ_g , is obtained from either

$$\log \sigma_g = \log (84\% \text{ size}) - \log (50\% \text{ size})$$

or

$$\log \sigma_g = \log (50\% \text{ size}) - \log (16\% \text{ size})$$

2.4 Acid Consumption

In experiments performed under flowsheet conditions (7), the amount of nitric acid apparently consumed in the first 4-hr leach at 25°C was generally between 10 and 20 moles per mole of uranium leached (Table 9a), as might be expected from the equations

and

With boiling acid, roughly 20-70 moles of acid apparently was consumed for each mole of uranium leached (Table 9a). Most of the nitric acid that appeared to be consumed probably was lost by evaporation through the condenser and not by reaction with the graphite since in the second leaches (Table 9b), where little uranium was recovered, the amounts of nitric acid apparently consumed divided by the number of moles of acid present initially were essentially the

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Fig. 5. Plots illustrating log-normal distribution of powders produced by disintegration of (a) unirradiated graphite-8% uranium fuel specimens in boiling nitric acid as a function of nitric acid concentration (4 hr digestion) and (b) irradiated graphite-uranium fuel specimens in 90% HNO_3 as a function of uranium content of fuel.

Table 9. Apparent Acid Consumption in Digestion of Uranium-Graphite Specimens with 90% HNO₃

Run No.	Temp, °C	U in Sample, %	Leaching Time, hr	Nitric Acid, moles			U Leached, moles	HNO ₃ Consumed	
				Init.	Final	Consumed		moles/ mole U	moles/ init. mole acid
a. First Leach Data Including All Washes Initial acid concentration assumed 21.2 M									
A-3	25	2.8	4	2.120	1.951	0.169	0.00325	52.	0.080
L1D		7.84		2.406	2.155	0.251	0.0104	24.1	0.104
B-5		11.7		2.311	2.140	0.171	0.0151	11.3	0.074
B-1		12.2		2.226	1.949	0.277	0.0153	18.1	0.124
B-2		13.7		2.438	2.179	0.259	0.0187	13.8	0.106
D1		16.7		1.162	1.068	0.094	0.0101	9.3	0.081
A-4	93	2.8	4	2.205	1.938	0.267	0.00346	77.2	0.121
2		3.72		2.391	2.058	0.333	0.00493	67.5	0.139
F-1D		6.38		1.119	1.009	0.110	0.00404	27.2	0.098
C-2		7.4		3.816	3.560	0.256	0.0162	15.8	0.067
B-4		11.8		2.260	1.892	0.368	0.0151	24.4	0.163
B-3		15.2		2.381	1.999	0.382	0.0206	18.5	0.160
D2		17.0		1.187	0.998	0.189	0.0107	17.7	0.159
14 ^a	93	0.00	24	2.420	2.107	0.313	-	-	0.129
C-3		7.3		4.229	2.975	1.254	0.0175	71.6	0.296
B-6		12		2.332	2.059	0.273	0.0155	17.6	0.117
B-7		12		2.459	2.075	0.384	0.0168	22.8	0.156
b. Second Leach Data Including All Washes									
A-3	25	2.8	4	2.120	1.914	0.206	0.000119	1731	0.097
L1D		7.84		2.406	2.327	0.079	0.000234	338	0.033
B-5		11.7		2.311	2.093	0.218	0.00030	727	0.094
B-1		12.2		2.226	2.116	0.110	0.000213	516	0.049
B-2		13.7		2.438	2.221	0.217	0.000289	751	0.089
A-4	93	2.8	4	2.205	1.975	0.230	0.000094	2447	0.104
2		3.72		2.391	2.139	0.252	0.000091	2769	0.105
F-1D		6.38		1.119	1.054	0.065	0.000383	170	0.058
C-2		7.4		3.880	3.495	0.385	0.000064	6016	0.099
B-4		11.8		2.247	1.993	0.254	0.000128	1980	0.113
B-3		15.2		2.385	2.063	0.322	0.000129	2500	0.135
14 ^a	93	0.00	24	2.420	2.107	0.313	-	-	0.129
C-3		7.3		4.229	3.667	0.562	0.000031	18,100	0.133
B-6		12		2.332	1.619	0.713	0.000116	6150	0.30
B-7		12		2.459	1.968	0.491	0.000135	3640	0.20

^a Volume of 90% HNO₃ comparable to those used in the experiments refluxed 24 hr.

same as in the first leach. For example, at 25°C, average values for this ratio were 0.095 and 0.072, respectively, for the first and second leaches although the amounts of uranium leached differed by a factor of about 50 (Table 9). Data were similar at the boiling point. About the same percentage of nitric acid was lost from a similar system containing no fuel specimen (Table 9b, run 14).

2.5 Off-gas Studies

A detailed study of the off-gases evolved during the reaction of fueled graphites with 90% HNO_3 has not yet been made. However, in preliminary experiments with prototype HTGR fuel containing 1.2% uranium and 14.3% thorium (supposedly as the dicarbides), the gas was mainly CO_2 , NO_2 , N_2O , and CO ; no hydrogen or hydrocarbons were detected. The total volume of gas evolved was not measured, but the $\text{CO}_2/\text{NO}_2/\text{CO}/\text{N}_2\text{O}$ mole ratios were $\sim 8.3/8.7/1.7/1$.

A systematic study of the reactions between uranium and thorium carbides and aqueous reagents has been started (19). Dissolution of UC in 6 M HNO_3 yielded mostly nitrogen oxides (20) and in 4 M HNO_3 mainly NO and CO_2 with traces of other nitrogen oxides and CO (21). Similar studies with more concentrated acid or with UC_2 and ThC_2 have not been made.

2.6 Preliminary Solvent Extraction Data (22)

Solutions resulting from the disintegration and leaching of uranium-graphite fuels with 90% HNO_3 may be adjusted to conditions for Purex solvent extraction by evaporating to a boiling point of about 135°C and then diluting with 3 vol of water. Boildown curves are being determined for uranium solutions containing 1-21 M HNO_3 . On a plot of nitric acid concentration vs. uranium concentration, the compositions resulting in a maximum boiling temperature lie on a straight line connecting azeotropic nitric acid (15.4 M) with about 1400 g of uranium per liter. Uranyl nitrate—nitric acid solutions which lie below this line yield boildown curves very similar to those previously reported for thorium nitrate—nitric acid solutions (23). The concentration of acid in the solution increases through a maximum, and then decreases down the maximum temperature line. When solutions with compositions above the maximum temperature line are boiled, the nitric acid concentration decreases rapidly until the composition approaches that of the line, and then it proceeds down this common line.

The effect of the trace amounts of colored organic compounds present in the leach solutions on the solvent extraction process has not been determined.

2.7 Reactions of Graphite with Nitric Acid

According to the literature, graphite reacts with nitric acid to produce carbon dioxide, nitrogen oxides, and a variety of water-soluble polycarboxylic acids intermediate to mellitic acid (24-28). These products are very similar to those obtained from reactions of nitric acid and other oxidants with charcoals, cokes, and coal (28-34). Juettner (24) states that in the oxidation of highly condensed organic materials with structures similar to graphite the carbon is converted mainly to CO_2 , only a small fraction going to mellitic acid. Most carbonaceous materials, when heated to about 1000°C , become graphitic in nature, and yield about the same amount of mellitic acid on oxidation (25).

When graphite is digested with 70-90% HNO_3 , the color of the solution initially is wine-red presumably due to the highly condensed organic materials in solution. However, as the graphite and dissolved species are oxidized more completely to mellitic acid, the color of the solution becomes lighter until, after about 2 weeks, it is straw-colored. Wine-red-colored solutions are also produced by reaction of uranium carbide with nitric acid (20,21); therefore the coloration of the leach solutions from fuels containing carbides can result from either source. The amount of carbon dissolved under flowsheet conditions was estimated from an experiment in which a piece of type AUC graphite was digested for 4 hr with boiling 90% HNO_3 . After removal of the undissolved graphite by filtration, the solution was evaporated to dryness on a steam bath. The red-colored solid residue from the evaporation, ~1.5 g per liter of leach solution, was completely water-soluble. The amount of solids isolated corresponds to 0.3 g of C per liter of leach solution if the solids are assumed to be mellitic acid. A more exact measurement of the amount of carbon in solution awaits development of a suitable analytical technique.

Although the kinetics of the reaction between graphite and nitric acid have not been studied, the rate appears to be very low even with finely powdered material. For example, after 2 weeks' contact of 100-g samples with refluxing fuming nitric acid (sp. gr. 1.5) containing 0.2% vanadic acid, about 75 g of

solid residue remained (24). The materials reacted were Acheson electrode graphite (-200 mesh) and "Dixon Micronized" graphite which was of an even smaller particle size. "Aquadag," a colloidal dispersion of graphite in water, was also reacted with the nitric acid—vanadic acid mixture for 2 weeks, at the end of which 21.5 g of residue remained per 100 g of dry material (24).

No evidence for the nitration of graphite was reported. Most of the studies were conducted with boiling solutions where oxidation rather than nitration is favored. At the higher temperatures, even the nitration products are often oxidized. Nitrations, therefore, are usually conducted at low temperature, often 0°C, to avoid destruction of the organic material by oxidation (35). Up to 5.8% nitrogen, mainly as nitro groups, can be introduced into bituminous coal by the action at room temperature of nitrating mixtures of concentrated sulfuric and nitric acids (34). However, if the mixture is warmed, oxidation sets in and the nitrogen content is decreased. Graphite nitrate can be made by treating graphite with 90-95% nitric acid; this reaction does not give the fully intercalated nitrate, but only the second stage (nitrate ion layers in every alternate inter layer-plane space) (36). Addition of N_2O_5 to 90-95% nitric acid causes graphite to turn blue and take up a full complement of nitrate layers. The dry graphite nitrate can be kept several days in sealed tubes without decomposition. On heating, it swells greatly, giving first a distillate and then oxides of nitrogen. Washing the compound with nitric acid (sp. gr. 1.48) brings about a rapid reversion to graphite. Washing with water or polar organic solvents also causes instantaneous decomposition of graphite nitrate (37). Because of the instability of the salt, it is extremely difficult to isolate.

In the oxidation of bituminous coal with alkaline permanganate, some phenolic compounds were isolated; however, it was concluded that the phenolic hydroxy groups were originally present in the coal or were produced by the breaking of ether linkages (30).

A graphitized fuel specimen containing 8% uranium was refluxed with 90% HNO_3 for 4.5 hr and the mixture was evaporated to dryness and strongly heated in a Bunsen flame (38). The acid boiled off rapidly, accompanied by moderate bumping and evolution of oxides of nitrogen. After the visible liquid had distilled,

white and brown (NO_2) fumes continued. The solid residue (graphite, uranium, organic oxidation products, and inorganic impurities) was strongly heated to redness (about 600°C) with no further fuming and no evidence of chemical reaction other than slow burning of the graphite.

2.8 Corrosion Data

Rates of corrosion of potential materials of construction in boiling 90% HNO_3 solutions have not yet been determined in this Laboratory. Several materials, including titanium and many of the stainless steels, appear adequate, at least for temperatures up to about 60°C (39).

3.0 COMBUSTION-DISSOLUTION PROCESS

3.1 Uncoated Uranium and Thorium-bearing Fuels

In duplicate experiments, uncoated, iron-free specimens HTGR-1 and -2 (Sect. 2.1.2) yielded combustion residues that dissolved readily in boiling 13 M HNO_3 —0.04 M NaF —0.1 M $\text{Al}(\text{NO}_3)_3$. After combustion of the graphite matrix at 800 – 900°C , the oxide ash was generally completely dissolved in less than 7 hr, yielding a solution containing about 1 M thorium.

3.2 Fuels Containing Pyrolytic Carbon-coated Particles

Samples of specimen HTGR-3 (Sect. 2.1.3), which contained pyrolytic carbon-coated uranium and thorium dicarbide particles, burned readily in a stream of oxygen. The mixed oxide ash was readily dissolved in fluoride-catalyzed nitric acid (see above).

3.3 Effect of Iron on Dissolution of Combustion Ash

Many of the fueled graphite specimens that contained up to 15% uranium also contained iron as an impurity (2), introduced possibly in the carbon flour or uranium compound used to fabricate the fuel or during such operations as ball-milling of the ingredients before molding. The iron oxide formed on combustion could not be dissolved in boiling 8 to 10 M HNO_3 in 24 hr. The residues dissolved completely in <4 hr in boiling 8 M HNO_3 —0.75 M HCl , but only when the HCl concentration was at least 0.75 M. In some cases, a small amount of residue that remained after dissolution of the ash in HNO_3 - HCl solution was shown by x-ray analysis to be SiO_2 .

Complete dissolution of the ash appears essential to avoid loss of uranium to the nitric acid--insoluble iron-bearing component. Uranium losses as a function of iron content have not yet been determined, but with a specimen containing 3.7% uranium and 0.1% iron, the loss to the iron-bearing residue was 0.2% after a 6-hr digestion of the combustion ash in boiling 10 M HNO_3 .

3.4 Fuels Containing Al_2O_3 -coated Particles

Combustion of Pebble Bed reactor (14) FA-22 specimens (Sect. 2.1.3) left the Al_2O_3 -coated UO_2 particles virtually unaffected. After burning in oxygen at 700-900°C and digestion of the ash in boiling 10 M HNO_3 for 8 hr, only 9.93% of the uranium was recovered.

3.5 SiC-coated Fuel Specimens

Combustion of fuel specimens coated with Si-SiC produced some nitric acid--insoluble material which retained uranium. The amount of uranium retained by the residue was proportional to the amount of SiC present, i.e., to the thickness of the coating. Pebble Bed reactor (14) specimens FA-6 and FA-8 were burned in a stream of oxygen at 700-900°C and the ashes digested with boiling 10 M HNO_3 for 6 to 8 hr. Uranium losses to the nitric acid-insoluble residue from the two specimens, one with a 3-mil coating and the other with a 30-mil coating, were 0.35 and ~2%, respectively. The samples contained 7-8% uranium; the U/Si weight ratios were about 4.5 and 0.33, respectively. Leaching of the ash from combustion of a 3-mil coated specimen (FA-6) with boiling 10 M HNO_3 -0.1 M HF instead of nitric acid alone decreased the uranium loss to about 0.2%.

3.6 Fission Product Behavior

In preliminary experiments with irradiated fuel, 0.001% burnup, to indicate the off-gas problems, Ru-106 volatilization was significant. From specimens containing ~3% uranium, 60-95% of the ruthenium was volatilized, but from specimens containing ~11% uranium only about 40% volatilized (Table 10). This difference in behavior cannot be explained at this time. Uranium, Zr-95, Cs-137, and Ce-144 were not volatilized.

Table 10. Distribution of Ru-106 in the Combustion of Uranium-Graphite Fuel Element Specimens

Exp. No.	U in Sample, %	Comb. Ash	Amount of Ruthenium in Indicated Sample, %					Total Volatilized
			Cool End of Tube	1st Scrub-ber	2nd Scrub-ber	3rd Scrub-ber	4th Scrub-ber	
1	2.98	40.1	59.8	0.1	0.06	-	-	59.9
2	3.04	5.7	94.0	0.2	0.07	0.02	0.005	94.3
3	2.88	8.5	91.3	0.08	0.06	0.02	0.01	91.5
4	10.9	62.0	37.8	0.1	0.03	0.007	-	38.0
5	11.8	53.2	46.5	0.1	0.1	0.02	0.009	46.8
6	11.4	59.6	40.4	0.04	0.02	0.006	-	40.4

The specimens, contained in porcelain boats, were burned in a furnace-heated 1-in.-dia quartz tube connected to four scrubbers, in series, containing 5 M NaOH. The distance from the combustion boat to the cool (100°C), exit, end of the tube was about 10 in., across which the temperature drop was at least 800°C. A Ca(OH)₂ bubbler at the end of the train showed that no CO₂ passed through the scrubbers. Six samples were analyzed for ruthenium: one from the dissolution of the combustion ash, one from the leaching of the exit end of the reaction tube, and one from each of the four scrubbers. Any ruthenium not found with the combustion ash was considered to have been volatilized.

3.7 Combustion of Graphite

A brief summary of the literature on the kinetics of the reaction between graphite and oxygen is presented here. The reader is referred to the excellent review articles by Binford (40), Walker, Rusinko, and Austin (41), and Prados (42) for more detailed discussion.

The reaction of graphite with oxygen not only is complex but also requires the simultaneous control of several variables if meaningful results are to be obtained. Some of the complications that have added to the confusion in interpreting the results of various workers are:

- 1) The effect of the oxygen partial pressure on the rate is not yet completely understood.
- 2) Both CO and CO₂ may be obtained as products.
- 3) The reaction may occur within pores as well as on the surface.
- 4) Traces of inorganic impurities (especially metals) strongly catalyze the reaction. Work with natural graphites is generally ignored by reviewers since these graphites usually contain at least 1% impurities.
- 5) Oxidation rates at low temperatures are accelerated by neutron and gamma radiation.
- 6) Rates may be retarded by the presence of certain halogen-containing substances in the gas phase.

Several distinct kinetic regions exist between 500 and 2000°C (40). Between 500 and 1000°C, both CO and CO₂ are formed and the order of the reaction is uncertain. Between 1000 and 2000°C, CO is the only primary product, and the reaction appears to be first order with respect to oxygen pressure. At high oxygen pressures the reaction may be diffusion-controlled. The rate of chemical reaction is very rapid above 800 to 900°C; however, the overall rate may be limited by the rate of diffusion and convection of reactant gases from the bulk of the gas stream to the external surface of the graphite. The reaction temperature, under these conditions, is not of primary interest. Probably of more importance is the flow of gas past the graphite surface since the rate of mass transfer of the reactants is strongly affected by the gas velocity. In the range 1200-1500°C, recrystallization of graphite causes hysteresis effects, and the reaction rate—temperature curve passes through a maximum.

The CO/CO₂ ratio increases with temperature according to the equation, given by Arthur (43),

$$\text{CO/CO}_2 = 10^{3.4} \exp(-12,400/RT)$$

Prados (42) correlated rate data for high-purity, artificial graphites by

$$k = 7.24 \times 10^9 \exp(-22,100/T)$$

where k has the units of weight fraction oxidized per hour per atmosphere of oxygen, and T , $^{\circ}\text{K}$. This correlation supposedly accounts for differences in sample size and geometry, oxygen partial pressure, and diffusional effects. Prados assumed that the rate was first order with respect to oxygen pressure and that the volume of gases produced (CO plus CO_2) was equal to the volume of oxygen which reacted. The correlation reproduces the measured reaction rates within a factor of 6. Prados also gives calculations on the approximate rate of heat release during combustion.

For a more detailed discussion of the effects of impurities and radiation on the rate of reaction, the review articles should be consulted (40,41). However, it should be mentioned here that the radiation effect is unimportant at temperatures above 500°C (42,44,45).

Carbon monoxide-oxygen mixtures can be explosive, particularly in the presence of water vapor which acts as a catalyst for the chain reaction (46). Dry mixtures can also be ignited if the source is sufficiently powerful. The explosive limits of CO -air and CO - O_2 mixtures are (47):

Mixture	CO Content, %		Ignition Temp, $^{\circ}\text{C}$
	Lower Limit	Upper Limit	
CO -air	12.5	74	650
CO - O_2	15.5	94	-

4.0 GRIND-LEACH PROCESS (3)

4.1 Uncoated Fuels Containing Uranium and/or Thorium

With ungraphitized fuel specimens containing ThO_2 or both ThO_2 and UO_2 as separate particles, thorium recoveries were $>99\%$ only when the ground specimens were leached with fluoride-catalyzed nitric acid (Table 11). Less than 3% of the thorium was recovered by leaching with boiling 15.8 M HNO_3 even when the specimens were ground finer than 200 mesh. Since the thorium had been fired to about 1400°C in fabrication of the specimens, the results are not surprising since sintered ThO_2 does not dissolve in boiling nitric acid without a fluoride catalyst (48). On the other hand, the uranium recovery,

Table 11. Recoveries by Leaching Ground Ungraphitized
Fuels Containing UO_2 and ThO_2

Fuel Comp, %		Particle Size, mesh	Leaching Agent	Recoveries, %					
U	Th			1st Leach and 3 Washes		2nd Leach and 1 Wash		Graphite Residue	
U	Th			U	Th	U	Th	U	Th
(a) UO_2 - ThO_2 as Separate Particles									
0	41.7	-10 +20	13 M HNO_3 -0.04 M NaF— 0.1 M $\text{Al}(\text{NO}_3)_3$	-	99.6	-	0.37	-	0.022
0	40.7	-10 +20	15.8 M HNO_3	-	1.75	-	0.46	-	97.8
0	42.6	-200	15.8 M HNO_3	-	1.62	-	0.92	-	97.5
2.6	23.0	-10 +20	13 M HNO_3 -0.04 M NaF— 0.1 M $\text{Al}(\text{NO}_3)_3$	93.5	97.7	5.7	1.5	0.67	0.80
2.6	22.3	-10 +20	15.8 M HNO_3	94.0	1.6	5.2	0.2	0.78	98.2
2.7	22.6	-200	13 M HNO_3 -0.04 M NaF— 0.1 M $\text{Al}(\text{NO}_3)_3$	96.3	98.9	3.5	1.0	0.33	0.088
2.8	22.4	-200	15.8 M HNO_3	97.7	0.61	2.0	0.33	0.33	99.0
(b) High-fired Co-precipitated UO_2 - ThO_2									
1.07	6.50	-10 +20	13 M HNO_3 -0.04 M NaF— 0.1 M $\text{Al}(\text{NO}_3)_3$	99.8	99.5	0.2	0.5	0.01	0.02
1.14	6.29	-10 +20	15.8 M HNO_3	0.6	0.4	0.4	0.1	99.0	99.5
1.24	7.72	-200	13 M HNO_3 -0.04 M NaF— 0.1 M $\text{Al}(\text{NO}_3)_3$	99.7	98.9	0.2	0.1	0.08	0.02
1.19	8.27	-200	15.8 M HNO_3	4.0	2.9	3.8	4.0	92.3	93.1

about 99.3% from the specimens containing about 2.6% uranium, was higher than expected from similar studies with graphitized fuels containing no thorium (2). The uranium recovery was independent of the thorium recovery (Table 11a).

With ungraphitized specimens containing about 1.1% uranium and 7% thorium, as co-precipitated oxide particles, both uranium and thorium could be recovered only by leaching with fluoride-catalyzed nitric acid (Table 11b). Two leachings of 10 to 20 mesh samples, 4 hr each, with boiling 13 M HNO_3 —0.04 M NaF—0.1 M $\text{Al}(\text{NO}_3)_3$ recovered >99.9% of the uranium and thorium. However, uranium and thorium recoveries were <8% when -200 mesh samples were leached with boiling 15.8 M HNO_3 .

With graphitized specimens containing 1.5% uranium and 7.2% thorium (HTGR-1), the uranium recovery, about 90%, was essentially that expected from studies with similar fuels containing no thorium (2). However, the thorium losses, 10-14%, were higher than expected, especially when the specimens were leached with fluoride-catalyzed nitric acid (Table 12). The presence of fluoride ion in the 15.8 M HNO_3 had no effect on thorium recovery. This behavior is unexplained at the present time.

Table 12. Recoveries by Leaching Ground Graphitized Fuels
Containing UO_2 and ThO_2 as Separate Particles

HTGR-1 specimens containing 1.5% uranium and 7.2% thorium

Particle Size, mesh	Leaching Agent	Recoveries, %					
		First Leach and 3 Washes		2nd Leach and 1 Wash		Graphite Residue	
		U	Th	U	Th	U	Th
-4 +8	15.8 M HNO_3	86.7	84.0	2.6	5.7	10.8	10.3
-16 +30	15.8 M HNO_3	84.0	82.8	6.1	4.1	9.9	14.2
-200	15.8 M HNO_3 —0.04 M NaF— 0.04 M $\text{Al}(\text{NO}_3)_3$	91.4	88.0	0.95	1.6	7.6	10.4
-200	13 M HNO_3 —0.04 M NaF— 0.1 M $\text{Al}(\text{NO}_3)_3$	86.4	84.3	1.3	3.0	12	13
-200	15.8 M HNO_3	92.8	88.7	0.6	1.4	6.8	9.9

4.2 Fuels Containing Coated Fuel Particles

Preliminary experiments were conducted with specimens FA-22 (Al_2O_3 -coated UO_2 particles) and HTGR-3 (pyrolytic-carbon-coated UC_2 - ThC_2 particles). As discussed in Sects. 2.1.3 and 3.4, neither the 90% HNO_3 nor the combustion-dissolution process was applicable to specimen FA-22. The combustion method was applicable to sample HTGR-3, but the 90% HNO_3 treatment was not. Grinding these samples to 200 mesh, to ensure crushing of the 125- μ fuel particles, and leaching with boiling nitric acid or fluoride-catalyzed nitric acid resulted in recovery of ~99% of the uranium and thorium:

Sample	Leaching Agent	Conditions	Losses to Graphite Residue, %	
			Uranium	Thorium
FA-22	15.8 M HNO_3	6 hr leach	0.99	-
HTGR-3	15.8 M HNO_3	Two 4-hr leaches	1.2	0.051
HTGR-3	13 M HNO_3 — 0.04 M NaF — 0.1 M $\text{Al}(\text{NO}_3)_3$	Two 4-hr leaches	0.65	0.036

Fine grinding of artificial graphites has already been studied (49).

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