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HEAD-END STUDIES OF SiC-COATED HTGR FUELS: UNIRRADIATED DRAGON COMPACT NO. 8232

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ORNL-TM-2389

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

HEAD-END STUDIES OF SiC-COATED HTGR FUELS: UNIRRADIATED DRAGON COMPACT NO. 8232

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FEBRUARY 1969

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HEAD-END STUDIES OF SiC-COATED HTGR FUELS: UNIRRADIATED DRAGON COMPACT NO. 8232

V. C. A. Vaughen

ABSTRACT

The first unirradiated Dragon fuel compact has been crushed, sieved, and subdivided into replicate portions to test for the fraction of silicon carbide-coated beads broken in handling and heavy-metal recoveries and losses in the crush-grind-leach flowsheet and in the crush-burn-grind-leach flowsheet. Standardized experimental techniques were devised for these tests. Both process flowsheets gave greater than 99.9% recoveries of heavy metals.

1. INTRODUCTION

With the cooperation of the Dragon Project, seven unirradiated and ten irradiated Dragon fuel compacts (burnup, ~ 16,000 Mwd/ton) have been received at ORNL. These fuel compacts are being used for studies of head-end processing steps (e.g., crushing, grinding, sieving, burning, leaching) and general chemical studies, such as off-gas released and retention of fertile, fissionable, and other radioactive species in the residues. It is anticipated that these studies will lay the groundwork for head-end studies of the American HTGR fuels, which are exemplified by the fuel proposed for use in the Gulf General Atomics Ft. St. Vrain reactor being built for the Public Service of Colorado. Both the Dragon fuel and the Ft. St. Vrain fuel contain $(Th, U)C_2$ fuel particles that are coated with pyrolytic graphite and silicon carbide and are embedded in graphite matrices.

Two fuel processing methods have been proposed and tested for HTGR fuels containing coated particles: the burn-grind-leach (or burn-grind-burn-leach) process[1-4, 5, 6] and the grind-leach process.[1-3, 7, 8] The burn-grind-leach process is the preferred method for processing Ft. St. Vrain type fuels. The major factor in

this choice is the necessity for separating the fissile $^{235}UC_2$ particles from the fertile ThC_2-$^{233}UC_2$ or ThO_2-$^{233}UO_2$ particles. Dragon and Peach Bottom type fuels contain a single fuel particle type and particle separation is not required; therefore, the grind-leach process appears to be applicable. However, previous work with irradiated Peach Bottom type fuels, using the grind-leach process, showed unacceptably high losses of heavy metals (~ 4%) and fission products (> 15%) in the residue;[7,8] with the burn-leach process, on the other hand, essentially quantitative recovery of heavy metals was achieved.[6]

The work reported here is designed to provide further information on: (1) the physical state of coated particle fuels after fabrication and irradiation (degree of particle breakage, etc.), and (2) the relative efficiency of alternative processing methods. For example, after burning the massive graphite matrix and separating and crushing the silicon carbide-coated particles, it may not be necessary to perform a second burning on the residue if the loss of heavy metals to the residual SiC and carbon is satisfactorily low (i.e., less than ~ 0.1%). The first series of studies reported here is designed to define these losses with unirradiated fuel in the absence of the second burning step. Further tests are planned with irradiated fuel samples.

2. COMPARISON OF DRAGON FUEL AND PROPOSED FT. ST. VRAIN FUEL

The Dragon fuel compacts used in our studies were thick-walled (0.44 in.) and thin-walled (0.25 in.) cylinders 1.75 in. OD by 2.81 in. long. The compacts contain a single-size range of particles of mixed thorium and uranium dicarbides (Th:U atom ratio = 10). These particles have protective coatings similar to those for the proposed Ft. St. Vrain fuel; however, the coating thicknesses are different. The Ft. St. Vrain reactor is an advanced thorium converter (Th/U = 4.25) and uses two types of fuel: one for startup and another for recycle. Data in Table 1 describe the fertile and fissile particles, and their coating thicknesses, for both fuels.

Table 1. Fort St. Vrain Fuel Particle Descriptions[a]

Reference	Fresh Fuel			Recycle Fuel			Dragon Fuel
	Fertile Particle	Fissile Particle 1	Fissile Particle 2	Fertile Particle	Fissile Particle 1	Fissile Particle 2	Compact 8232 Standard Fuel
Particle Number	1	2	3	1	4	3	-
Kernel Composition	ThC_2	$(Th, {}^{235}U)C_2$	$({}^{235}U)C_2$	ThC_2	$(Th, {}^{233}U)O_2$	$({}^{235}U)C_2$	$(Th, {}^{235}U)C_{2.4}$
Kernel Diameter, μ	400 ± 100	200 ± 50	100 ± 10	400 ± 100	400 ± 100	100 ± 10	457
Buffer Carbon Thickness, μ	50 ± 10	50 ± 10	100 ± 10	50 ± 10	50 ± 10	100 ± 10	~ 20
Inner Isotropic Pyrocarbon Thickness, μ	20 ± 5	20 ± 5	20 ± 5	20 ± 5	20 ± 5	20 ± 5	~ 5
Silicon Carbide Thickness, μ	20 ± 3	20 ± 3	20 ± 3	20 ± 3	20 ± 3	20 ± 3	17
Outer Pyrocarbon Thickness, μ	40 ± 5	30 ± 5	30 ± 5	40 ± 5	40 ± 5	30 ± 5	57
Total Particle Diameter, μ	660 ± 146	440 ± 96	400 ± 56	660 ± 146	660 ± 146	440 ± 56	655

[a]Particles will be bonded into fuel sticks for insertion into graphite hexagonal block fuel elements. Natural boron carbide sticks containing about 15% B_4C in a graphite matrix will be used in first core fuel elements as a burnable poison. In subsequent cores boron carbide will be incorporated into the particle matrix material.

The Dragon fuel is seen to be similar in size to the fertile particle number 1 (Table 1) proposed for the Ft. St. Vrain reactor. All the techniques and the steps required for processing the Ft. St. Vrain fuel (except for particle size separation) can be worked out by using Dragon fuel as a model.

3. GENERAL EXPERIMENTAL PROCEDURE

The experimental procedure can be divided into four steps: (1) size reduction of the original compact (1.75 in. OD by 2.81 in. long) by crushing, (2) limited sieve analysis, (3) splitting the middle cuts to obtain replicate sample aliquots (see Appendix), and (4) processing studies on the individual sample aliquots.

The size reduction (crushing) studies are important since the actual Ft. St. Vrain reactor fuel consists of small coated particles dispersed in large graphite elements, or "logs". These large logs will probably need to be subdivided as a first step in a recovery process. Particle breakage will be important both from process loss and from waste handling standpoints. The flowsheet for crushing and sieving the Dragon reactor fuel compacts is given in Fig. 1.

The limited sieve analysis gives an estimate of the frangibility of the graphite matrix, an estimate of the mean particle size and of the size distribution, and may suggest a means for separating fertile from fissile particles. In addition, study of the smallest fractions (which can only contain fractured particles and graphite dust) provides an estimate of particle breakage during handling. The largest lumps serve well for metallographic studies and chemical analysis of the original fuel.

The remaining sieve fractions (+9, +20, +42) were combined and split into replicate samples. Three passes through a two-way splitter were made, generating eight samples (Fig. 2). These samples are ordered by weight and then randomized into replicate pairs (to minimize size or density bias and to increase confidence in the sample data).

To study particle breakage in handling, one needs an estimate of the degree of breakage present within the original fuel matrix. One pair of samples was carried

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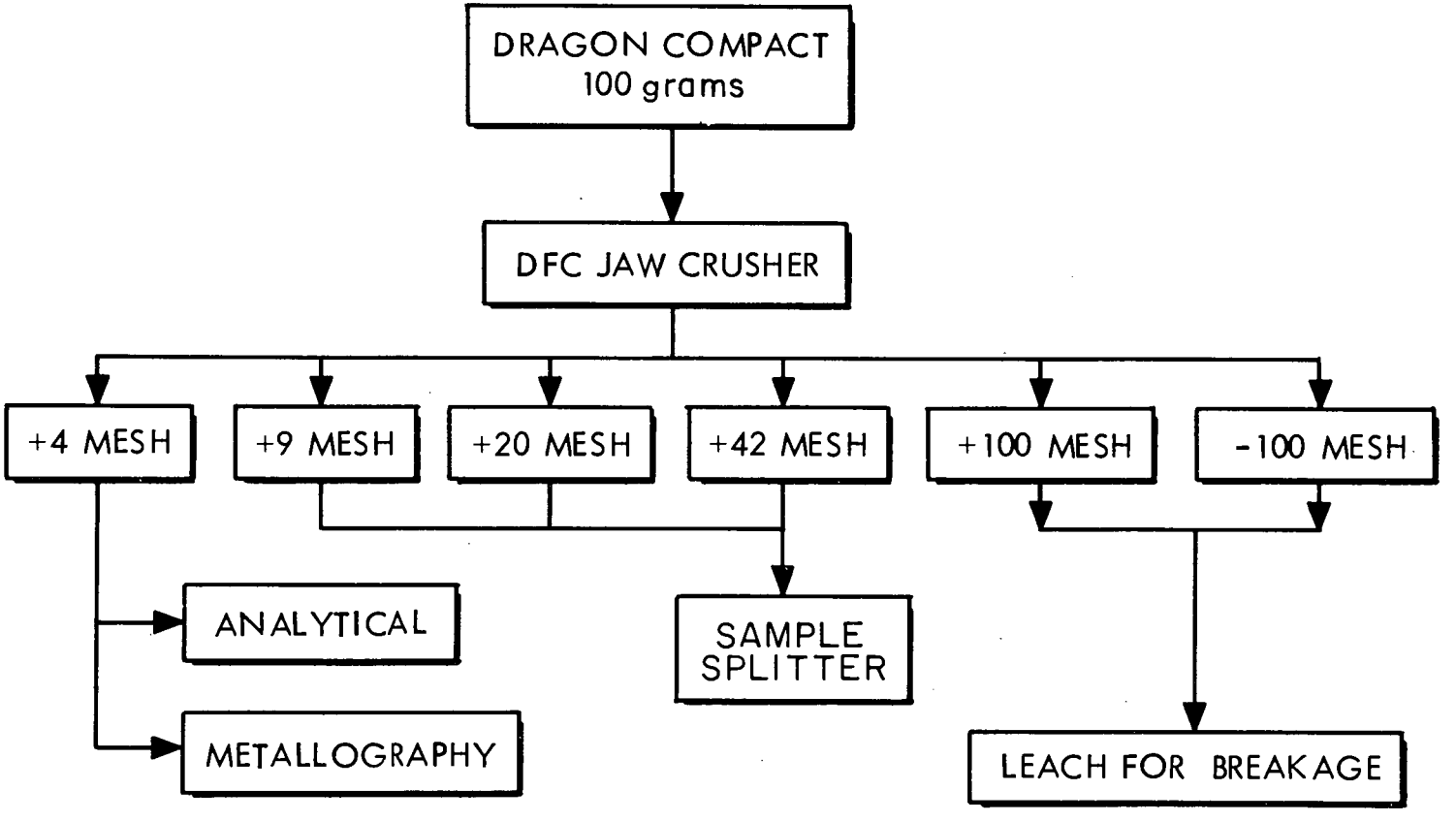

Fig. 1. Crushing and Sieving of Dragon Fuel.

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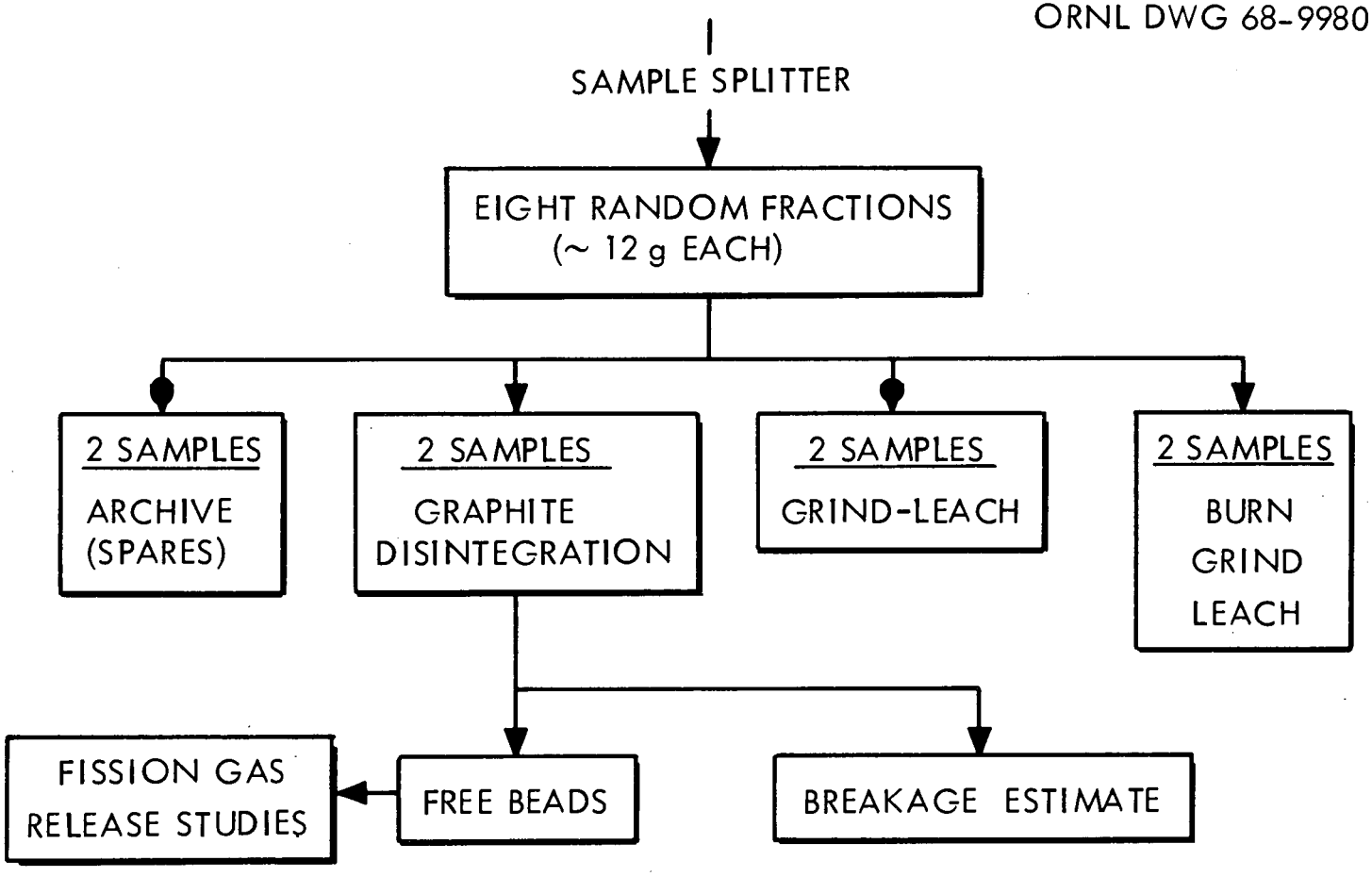

Fig. 2. Sampling for Head-End Studies of Dragon Fuel.

separately through a graphite disintegration step utilizing white fuming HNO_3 to release particles, and Thorex process dissolver reagent to dissolve any cores exposed because of SiC coating breakage. The pyrolytic carbon-coated beads were left free in a sludge of graphite. Any broken particles should be leached under these conditions. The pyrolytic-carbon-coated fuel particles were recovered from the leached sludge by dry sieving. Irradiated particles treated this way may be used for off-gas release studies. The dried sludge was burned in a combustion boat and leached in order to check on the completeness of leaching and residue retention.

The crush-grind-leach flowsheet is shown in Fig. 3. Two of the samples of crushed fuel were ground to -60 mesh in a Waring blender and leached with Thorex reagent [13 M HNO_3--0.05 M HF--0.1 M $Al(NO_3)_3$]. The residues were carefully washed and analyzed for losses.

The crush-burn-grind-leach flowsheet is given in Fig. 4. Two of the samples were burned separately in a fluidized-bed burner (using Al_2O_3), and sieved to separate fissile particles from broken particles and Al_2O_3. The fissile particle fractions were ground separately to -60 mesh (< 0.250 mm) and leached. The fines and Al_2O_3 were leached. One can obtain data on heavy metal recoveries and losses and particle breakage during fluidized-bed burning.

The final two samples were held as archive samples (or spares) to help resolve questions after the data are in hand. (One was burned to test a new fluidized-bed burner design.)

4. CRUSHING AND SIEVING STUDIES OF UNIRRADIATED DRAGON COMPACT NO. 8232

4.1 Purpose

Our objective was to develop a standard crushing procedure for thick-walled (0.44 in.) and thin-walled (0.25 in.) Dragon compacts (cylinders 1.75 in. OD by 2.81 in. long), using a DFC Model 20830 jaw crusher modified for dc motor drive.

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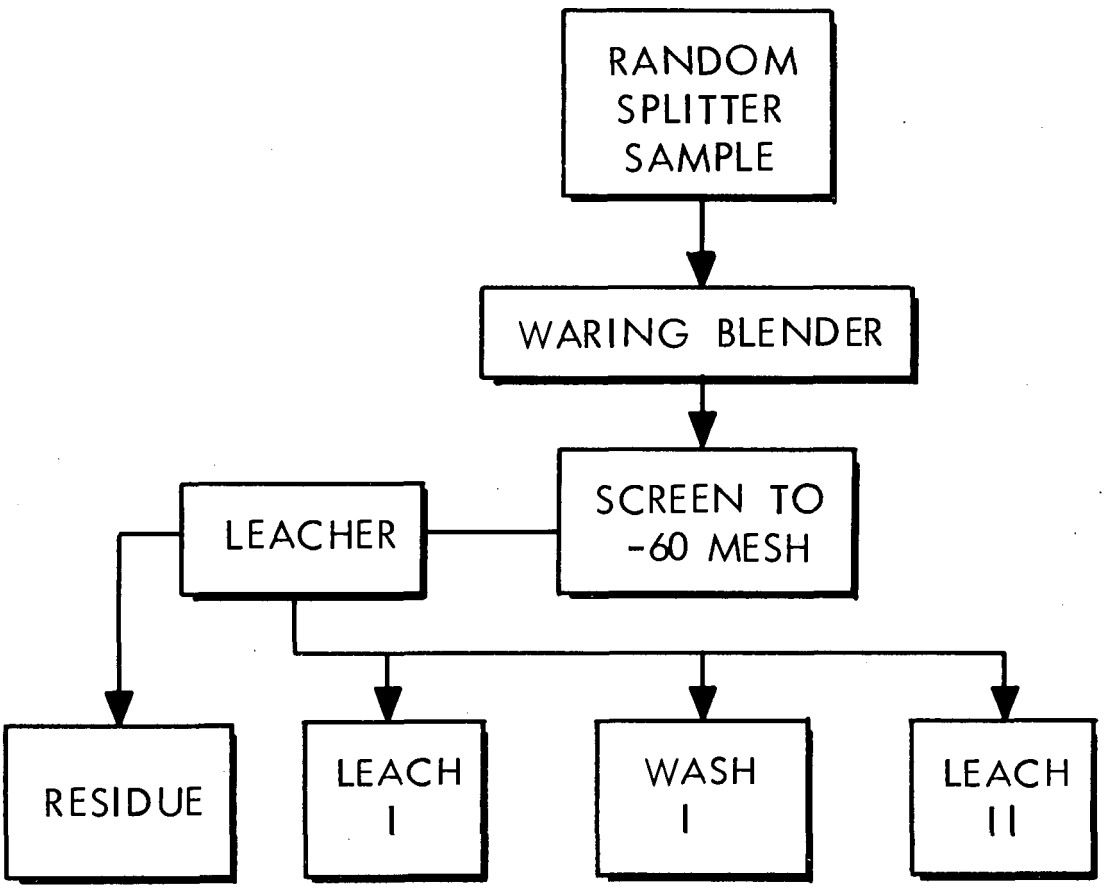

Fig. 3. Crush-Grind-Leach Flowsheet for Dragon Fuel.

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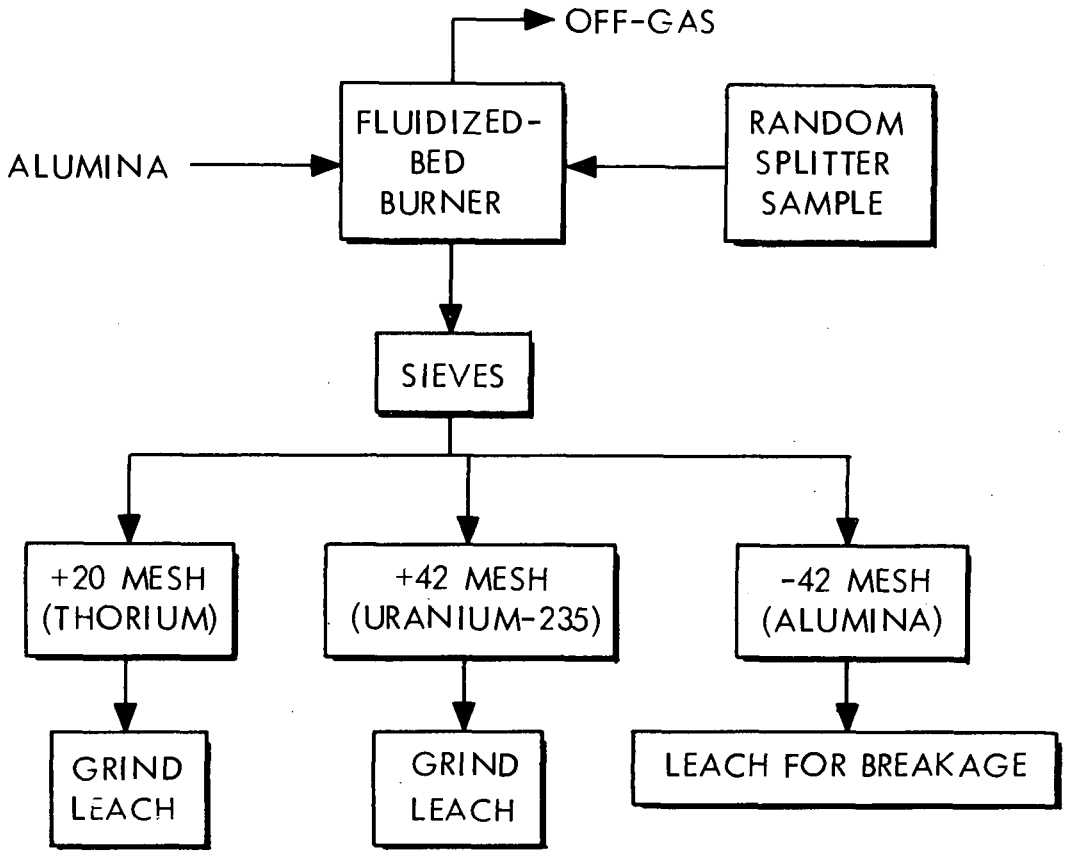

Fig. 4. Crush-Burn-Grind-Leach Flowsheet for Dragon Fuel.

4.2 Experimental Procedure

Synthetic compacts in the form of hollow cylinders were machined from graphite bar stock to Dragon fuel specifications in order to develop crushing techniques and to provide a basis of comparison. These synthetic compacts were crushed in the DFC Laboratory Model 20830 jaw crusher in five sequential experiments. In every case the crushing was performed in two passes through the machine. Variables studied were crusher jaw opening size and orientation of compact during rough crushing. The crusher products were passed through five sieves to obtain a rough size distribution.

4.3 Results

The hollow cylinders tended to break into long splinters (1/4 in. by 1/2 in. long) when crushed in a straightforward manner (cylinder axis parallel to the jaws). More symmetrical lumps were obtained by feeding the compact crosswise or vertically into the crusher. The results of the crushing and sieving studies for vertically fed compacts are presented in Table 2.

Table 2. Crushing and Sieving Studies for Synthetic and Dragon Fuel Compacts

Values are expressed as % of total recovered from the sieves.

	Percentage in the Sieve Fractions					
Description	+4	+9	+20	+42	+100	-100
Synthetic Fuel Compact[a]	5.67 ±1.12[b]	66.90 ±3.80[b]	12.37 ±0.62[b]	5.63 ±0.71[b]	4.27 ±1.07[b]	5.13 ±2.00[b]
Dragon Compact No. 8232	4.0	61.7	9.0	17.7[c]	2.9	4.7

[a]Contains no beads.

[b]95% confidence level, "t" distribution.

[c]Large number of free beads.

4.4 Discussion and Conclusions

The standard procedure adopted for operating the jaw crusher involved feeding the compacts vertically into a wide-open crusher (~ 5/8-in. opening at the bottom) for the first pass. The jaws were then shimmed to about 1/16 in. for the second pass. Initial, intermediate, and final total weights were measured. The product was sieved through screens of 4, 9, 20, 42, and 100 mesh, and each fraction was weighed to obtain the size-vs-weight distribution.

5. ESTIMATION OF BEAD BREAKAGE DURING CRUSHING

5.1 Experimental Procedure

Two large lumps (1.67 g) suitable for analysis were removed after the first crusher pass. The remainder of the material was crushed the second time at the 1/16-in. spacing. The crusher product was sieved and weighed as described above.

The two fines fractions (± 100 mesh) were burned separately in a combustion boat and leached. For simplicity (and since there was no difference between them), they are reported as one combined fraction. The composite sample (8.74 g) was burned, leaving a residue of 0.546 g; the residue was leached and rinsed by the standard procedure. An unburnt, insoluble residue (0.0768 g) was sampled.

5.2 Results

The results of leaching the fines generated during the crushing step are given in Table 3. The fines fraction (± 100 mesh, 8.74 g) did show signs of segregation, and the amount of bead breakage was calculated by four means: uranium balance, thorium balance, residue weight (Si),and carbon balance. These results are also shown in Table 3.

The fines (7.5% of the total weight of the compact) contained only 2% of the uranium and thorium. The final residue, after leaching, had the appearance of sand rather than of shells of SiC. Assuming that all the SiC was converted to SiO_2 in the final residue, about 2% bead breakage was indicated.

Table 3. Estimates of Dragon Compact Bead Breakage

Composition	Calculated (g)	Recovered from Fines[c] (g)	(%)	Recovered by Graphite Disintegration (%)	Total Breakage (%)
Total	116.93	8.74	7.5	-	-
U	1.85	0.041	2.2	0.7	2.9
Th	17.69	0.333	1.9	0.8	2.7
C	92.39	8.2	8.9	-	-
Si[a]	2.40	0.077	3.2	-	-
Si[b]	3.60	0.077	2.1	1.6	-

[a]SiC basis.
[b]SiO_2 basis.
[c]± 100 mesh fractions.

A carbon balance based on 2% bead breakage plus extra finely pulverized matrix graphite indicated that 8.3 g of total carbon was present in the combined fines fraction. The measured weight loss on burning was 8.2 g. Results from the next section (graphite disintegration) are also included in Table 3 to complete the particle breakage results.

5.3 Summary

Approximately 1.5% of the compact was lost in handling; about 7.5% of the compact was crushed to less than 42 mesh. However, only about 3% of the beads were broken.

6. DETERMINATION OF THE AMOUNT OF BROKEN BEADS IN THE -4 TO +42 MESH FRACTIONS (BY FUMING HNO_3 DISINTEGRATION OF THE GRAPHITE MATRIX)

6.1 Purpose

The purpose of this work was to determine the status of fuel bead integrity in the middle size (-4 to +42-mesh) fractions of the crusher product by a method other than burning. This experiment provides a basis on which to estimate bead breakage in the fluidized-bed burner.

6.2 Procedure

Two fractions (R3, R6) obtained from the splitter were leached separately with 50 ml of white fuming HNO_3 for 3 hr at reflux. The residue was washed with two 25-ml portions of water. The combined first leach and two washes were mixed and submitted in duplicate samples. A third 25-ml rinse (W-1) was submitted separately. This is the standard procedure used in each leaching test.

The leaching and washing were repeated (L-2) with 50 ml of Thorex dissolver reagent [13 M HNO_3, 0.1 M Al, 0.05 M HF].

A third 3-hr leach with white fuming HNO_3 was performed. The residues were sieved through a 42-mesh sieve. The +42-mesh beads were retained. The -42-mesh fines were burned in a combustion boat and submitted as residue samples (0.0062 g).

6.3 Results

The graphite disintegration results are given in Table 4. The +42-mesh product contained some small graphite lumps as well as the free beads. The lumps appeared to be free of beads.

The -42-mesh graphite "flour" burned away, leaving 6 mg of fine white powder.

The solution resulting from the graphite destruction contained 50 to 100 mg of carbon per liter. About 80 to 90% of the heavy metals accounted for (0.7 to 0.8%

Table 4. Fuming HNO_3 Disintegration of Graphite From Dragon Compact No. 8232

Fraction	Component	Calculated (g)	Total Measured (g)	Recovered by Leaching (g)	Final Residue (g)
R3	Weight	10.375	10.376	-	6.2×10^{-3}
	U	0.174	0.00121	0.00108[c]	1.3×10^{-4}
	Th	1.664	0.0124	0.0112[c]	12×10^{-3}
	SiC	0.226	-	-	5.3×10^{-3}[d]
	Total coated particles	3.051	3.944[a]	-	-
	Matrix Graphite	7.323	5.842[b]	0.009[c,e]	-
R6	Weight	10.713	10.717	-	6.2×10^{-5}
	U	0.180	0.0013	0.0013[c]	-
	Th	1.719	0.015	0.015[c]	-
	SiC	0.233	-	-	-
	Total coated particles	3.151	4.110[d]	-	-
	Matrix Graphite	7.562	5.950[b]	0.005[e]	-

[a]+42-mesh particles.

[b]-42-mesh powder.

[c]Average of analyses from two laboratories.

[d]SiO_2.

[e]Soluble carbon from leaching.

of the total sample) were present in the first leach. An additional 2 to 5% was recovered in the wash and second leach. Based on the analysis of one 6-mg residue, about 10% of the heavy metals were present in the -42-mesh residue. (This residue was not leached after burning.)

6.4 Discussion of Results

The graphite destruction may not have been complete in six hours of leaching

with white fuming HNO_3. Broken particles exposed on fracture surfaces were probably adequately leached, and the results should be a valid indication of the amount of fuel breakage due to the crushing procedure. The total of heavy metals recovered from the combined 100-mesh fines fraction (~ 2%) and the additional heavy metals recovered by the graphite destruction experiment (~ 0.7%) indicate a total bead breakage (by this crusher) of between 2 and 3%.

Although the amount of residue was quite small (~ 6 mg) from the burning of the -42-mesh graphite flour, it contained about 1.5 mg of heavy metal as oxides. Assuming 1% bead breakage, the residue should contain about 3 mg of SiO_2 (found by difference = 4.5 mg).

6.5 Conclusions

The crushed Dragon compact No. 8232 suffered about 3% bead breakage in the crushing procedure. About two-thirds of the broken particles were originally -42 mesh.

The graphite disintegration procedure did not completely disintegrate the graphite; however, the beads appeared to be separated from the few remaining lumps of graphite on the +42-mesh screen. The major fraction of the graphite was reduced to a -42-mesh powder. The procedure is adequate for the purposes of exposing and leaching broken fuel particles.

7. CRUSH-GRIND-LEACH STUDIES OF DRAGON COMPACT NO. 8232

7.1 Purpose

The purpose of these particles was to determine the effectiveness of the crush-grind-leach head-end process.

7.2 Procedure

Two samples (R5, R7) of crushed, unirradiated Dragon Compact No. 8232 were ground separately to -60 mesh in a Waring blender with carbide-tipped blades.

Products from the blender were leached twice, separately, by the standard leaching procedure with Thorex dissolver reagent. The residue was washed, dried, and weighed.

Solution and solid samples were analyzed.

7.3 Calculations

The handling and solubility losses can be estimated by calculating the weight of material that should be present in each step. There is one complication; the (Th, U)C_2 hydrolyzes in air to form oxide products. No atmosphere control was attempted, nor was complete reaction sought. The following simplifying assumptions were made:

1. All dicarbide material reacts to form U_3O_8 and ThO_2.
2. All "carbide" carbon escapes as gases.
3. There is no significant weight gain or loss as a result of the increased surface area of the graphite matrix after grinding.
4. All heavy metals are extracted, and the dried insoluble residue contains all the buffer coating (IPYC), silicon carbide coating (SiC), and isotropic pyrolytic carbon (OPYC), and matrix graphite from the original fuel.

Assumptions No. 1 and No. 2 (above) really affect only the weight of the fuel when it is poured from the blender. If No. 1 is not satisfied, the weight will be less than calculated. If No. 2 is not satisfied, there will be a tendency for the material to weigh more than calculated. However, leaching should ensure essential completion of the reactions described in No. 1 and No. 2, if the nongaseous products from No. 2 are soluble. Consequently, the final weight after leaching will reflect total handling losses and the loss due to solubility of the carbonaceous materials in (or by chemical action of) nitric acid.

The tabulated data in Table 1 of the Appendix serve as a convenient starting base for calculation. The change in weight due to hydrolysis was calculated by subtracting the weight of sample present as carbon in the (U, Th)C_2 compound (extra graphite in the kernel was assumed to be unaffected) and adding the weight of oxygen

calculated as U_3O_8 and ThO_2. All heavy metals were extracted by leaching, leaving only carbon and SiC residues. The calculations and measured weights are compared in Table 5.

Table 5. Comparison of Calculated and Measured Weights for Crush-Grind-Leach Samples

		Hydrolysis	Blender Product	Leaching	Residue
R-5					
Calculated, g	14.0285	+0.0974	14.126	-2.840	11.286
Measured, g	14.0285		14.150		10.575
Difference, g (calculated - measured)	0		-0.024		+0.711
% of calculated			100.2		93.70
R-7					
Calculated, g	13.0345	+0.0905	13.125	-2.639	10.486
Measured, g	13.0345		12.952		9.804
Difference, g (calculated - measured)			+0.173		+0.682
% of calculated	100.00		98.68		93.50

The difference in weight measured and weight calculated for the blender product may indicate a lack of complete reaction. However, since the magnitude of the difference is about twice the theoretical weight change, it may represent the physical loss of 0.5 to 1% of the material. The excellent agreement between measured and calculated values for the R-5 is considered to be fortuitous.

The calculated fuel values from the leached residues (0.218 g U, 2.093 g Th) were adjusted for a 1% loss in sample R-7 before leaching.

It is significant that both residues were essentially the same weight fraction of the calculated weight; if this result continues in other samples, this test may point to

a significant way of estimating the loss due to solubility. The heavy metals content will not be adjusted since the loss can be assumed to be independent of the uranium and thorium recoveries; the loss must occur, then, either via solubility or via handling after leaching.

7.4 Results

The amounts of uranium and thorium recovered in the leaches and found in the residues are listed in Table 6. Comparisons are indicated for both samples R5 and R7.

Table 6. Crush-Grind-Leach Studies of Dragon Compact No. 8232; Material Balance on Leach Solutions and Residues

Sample	R5U	R7U	R5Th	R7Th
Feed calculation, g	0.235	0.216	2.251	2.072
Total measured, g	0.251	0.226	2.290	2.192
Total measured output basis, %	100	100	100	100
L-1,[a] %	99.58	99.68	99.13	99.20
W-1,[b] %	0.17	0.08	0.09	0.04
L-2, %	0.24	0.20	0.71	0.70
Residue, %	0.02	0.04	0.07	0.06

[a]L = leach solution content.
[b]W = wash solution content.

Generally, more was recovered (by up to ~ 6%) than calculated. The biggest source of heavy metals was the first leach, which contained an average of more than 99% of the total heavy metals. Residue loss was 0.05% (average).

7.5 Conclusions

The grind-leach process recovered more than 99.9% of the uranium and thorium in unirradiated Dragon compact No. 8232. About 6% of the graphite was lost and may have been destroyed or dissolved by the acid refluxing action.

8. CRUSH-BURN-GRIND-LEACH STUDIES OF DRAGON COMPACT NO. 8232

8.1 Purpose

Our objective in these studies was to study the crush-burn-grind-leach head-end process.

8.2 Procedure

Three fractions of crushed fuel from compact No. 8232 (R2, R4, R8) were burned with alumina in fluidized-bed burners. Two fractions (R4, R8) were burned in a cylindrical-walled burner (No. 1), and one (R2) was burned in a conical-walled burner (No. 2). The conical-walled burner was superior. In each instance the burner was cooled and the bed was inspected periodically to determine the amount of unburned carbon.

The burner was operated in a furnace set at 750°C, and temperatures in the bed were varied from 680°C to 780°C, depending on the oxygen feed rate and the carbon remaining. The burning zone was located at the top of the bed in burner No. 1 and throughout the bed in burner No. 2.

Gas flow rates were varied between runs. Nitrogen flow rates (STP) of 0, 780, and 1680 ml/min were used with oxygen flow rates (STP) of 0, 225, and 450 ml/min with 2 to 3 psig back-pressure in the burner. Burning conditions are given in Table 7.

After essentially all the carbon had been burned off, the entire bed was dumped out, weighed, and sieved on a 42-mesh screen. In each run the alumina and any carbon fines passed through the screen, leaving the unbroken SiC-coated fuel particles behind. The alumina beds from Runs R4 and R8 were leached to determine the fraction of bead breakage.

The R4 and R8 beads were crushed in a carbide-tipped Waring blender until all the material passed a 60-mesh sieve. In both cases, the crushed material was pyrophoric (in air), and burned like charcoal. The burnt residue was leached with Thorex dissolver reagent. Samples of leaches and residues were analyzed.

Table 7. Summary of Burning Conditions for Fractions R2, R4, and R8 of Dragon Compact No. 8232

Sample No.	Weight of Fuel Charge (g)	Weight of Al_2O_3[d] (g)	Maximum O_2 Flow (STP) (ml/min)	N_2 Flow (STP) (ml/min)	Total Fluidizing Velocity at 740°C and 3 psig (fps)	Settling Velocity at 740°C and 3 psig (fps)	Maximum Carbon Burning Rate (g/min)	O_2 Utilization[a] (%)
R4[b]	11.942	15.197	450	1680	3.2	0.7	0.24	14
R8[b]	13.004	15.011	225	0	0.3	0.006	0.12	54
R2[c]	15.502	15.160	225	780	1.2	0.3	0.12	49

[a] $\frac{\text{Moles carbon burned (as } CO_2)}{\text{Moles oxygen used (as } O_2)} \times 100$

[b] 0.62-in.-ID fluid bed.

[c] Conical fluid bed.

[d] -80 +100 mesh (screened).

8.3 Calculations

The many steps involved in this process require that material balances for total weight and Al_2O_3 be calculated for the burner and sieve systems. Weights measured at each step are used to calculate the losses due to handling, the amount of carbon burned off, and the inventory of heavy metals surviving to the grind-leach step.

The calculated values are included with the run data in Table 8. Results of the material balance-simultaneous equation calculations are compared with calculated results derived from assumptions as to original fuel composition and equipment behavior. The prior estimate (0.7%) of the broken beads that remain with the larger lumps was used to calculate the extent of the bead loss to the alumina. This same estimate, plus a 1% handling loss, was used in determining the amount of beads that survive to the +42-mesh fraction. External carbon burning was assumed to be 95% complete. The core graphite, and IPYC and SiC shells were assumed to survive the smoldering fire and leaching.

8.4 Results

The leaching results and residue analyses for both the R4 and R8 fractions are presented in Table 9. The calculated heavy metal inputs are compared with the sum of all heavy metals found in the residues and leaches (output).

8.5 Discussion of Results

8.5.1 Burner Behavior

The cylindrical burner (0.62 in. ID) had a hot spot at the top of the bed, indicating that the carbon was burning above the alumina. In addition, it required burning for a total of 4 hr (three heats) to remove the bulk of the carbon. A laboratory conical glass vessel indicated that an alumina spouting bed would distribute the carbon fines throughout the alumina bed. The conical burner had a uniform bed temperature during burning. It required two heats (total 3.5 hr) to reduce the carbon content significantly.

Table 8. Burn-Grind-(Burn)-Leach Studies of Dragon Compact No. 8232; Material Balances for Products and Residues

Sample	Fuel + Alumina (g)	Burner Product (g)	Sieve Product (g)	Carbon Burned Off[a] (g)	Handling Loss[a] to Burner and Sieve (g)	+42-Mesh Beads (g)	-42-Mesh Alumina (g)	+42-Mesh Residue (g)	-42-Mesh Residue (g)
R1	30.662			10.61	0.08	4.240	15.725		
(Measured/Calculated)[b]	(100.0%)			(94.2%)		(119%)	(101%)		
R4	27.139	18.301	18.291	8.67	0.18	3.082	15.209	0.646	14.948
(Measured/Calculated)	(100.0%)	(100.0%)		(100.0%)		(112%)	(98.0%)	(134%)	
R8	28.015	18.692		9.17	0.19	3.650	15.042	0.976	14.758
(Measured/Calculated)	(100.0%)	(101.5%)		(97.1%)		(122%)	(97.8%)	(186%)	

[a]By material balance and solution of simultaneous equations.

[b]Assumptions: 95% carbon burned off: 1% fluid-bed product lost in handling; 1% of beads broken to -42 mesh in original sample; British Particle data; -42 residue was not burned, i.e., it contained all core graphite, IPYC, and SiC (no "carbide" C).

Table 9. Burn-Grind-(Burn)-Leach Studies of Dragon Compact No. 8232; Results of Leaching and Analyses of Residues for R4 and R8 Fractions

Step	R4 U	R8 U	R4 Th	R8 Th
Feed Calc., g[a]	0.200	0.218	1.916	2.086
Total Output, g	0.189	0.237	1.75	2.08
Total Output, %	100	100	100	100
+42-mesh product	99.52	99.33	99.30	99.20
-42-mesh product	0.41	0.64	0.55	0.74
+42-mesh residue	0.009	0.02	0.08	0.04
-42-mesh residue	0.06	0.006	0.07	0.02
Total Losses,[b] %	0.069	0.026	0.15	0.06

[a]Not adjusted for an estimated 1% handling loss in burner.

[b]As unleachable residues.

8.5.2 Solids Handling and Losses

The data of Table 8 indicate that good control of solids was experienced in these runs. About 1% of the fluid-bed product was apparently lost during handling. The fire that occurred after sample R4 was blended prevented determination of a loss; however, the weight prior to blending was essentially equal to that after the fire. Since one expects a weight gain of 0.074 g by converting $(U, Th)C_2$ to $(U, Th)O_2$ in this step, one may say that about 0.074 g may have been lost in handling. This is about 2% of the blender product. No data correction was made for this loss. In the case of fraction R8, the fire did not occur until after weighing. A weight loss of 0.024 g (0.6%) was measured. No correction was made. Sample R2 was not blended. In neither case was any attempt made to complete the burning beyond the natural event.

An interesting observation can be made, based on fuel material found in the recovered beads and in the final leached bead residue. Analyses of these samples gave between 15% and 25% more weight of silicon carbide-coated particles (for the

predicted heavy metals) than the weight calculated from the British data. The leached residues were 30 to 90% heavier than calculated.

8.6 Recoveries

Recoveries, as measured by percentages of all material found in the leaches and leached residues, appeared to be quite similar for the various samples.

About 0.6% of the heavy metals were found in the alumina bed fraction. This value agrees well with estimates of broken beads in the larger size fraction furnished by the burning-nitric acid graphite destruction studies (Table 3).

The overall process losses (insoluble material in the residues) were found to average less than 0.1% (about 0.05% U and 0.1% Th in these tests).

8.7 Conclusions

The burn-grind-(burn)-leach head-end experiments on the unirradiated Dragon Compact No. 8232 indicate:

1. The average overall heavy-metal recoveries are 99.9% or better.
2. Bead breakage is nil during fluidized-bed burning under conditions ranging from quiescent burning to a 3.2-fps fluidizing velocity under the run conditions.
3. The alumina (and residual carbon fines) are easily separated from the SiC-coated beads by sieving.
4. The alumina bed contained only the small amount of heavy metals originally present in broken particles.
5. The pyrophoric burning is not considered a good test of burning after crushing.

9. SUMMARY

The procedures for our studies of the crushing, splitting, grinding, leaching, and fluidized-bed burning of Dragon Compacts are now considered to be standardized. The graphite disintegration step does not completely separate all the matrix graphite from the pyrolytic-carbon-coated spheres (some remains as +42-mesh lumps); however, the matrix graphite is free of spheres.

Both the crush-grind-leach and the crush-burn-grind-leach head-end treatments resulted in recovery of more than 99.9% of the heavy metals from the unirradiated "standard" Dragon compact No. 8232.

Bead breakage during crushing was about 3%. No other significant source of bead breakage was found in the work with this unirradiated standard compact.

The heavy-metal analyses and the weights of fuel used in the crush-burn-grind-leach and crush-grind-leach head-end processes were combined to give an estimate of the fuel loading for the as-received compact. A total of 52.008 g of fuel contained 0.908 g of uranium and 8.307 g of thorium. By using a weight ratio, the combined middle cuts are estimated to contain 1.79 g of uranium and 16.39 g of thorium, as compared with corresponding calculated values of 1.722 g and 16.464 g. This is considered to be excellent agreement.

10. APPENDIX

Calculation of the Starting Materials in the Dragon Compact No. 8232

Fuel Parameters, General Procedure

The initial fuel composition was calculated from British-supplied basic data and estimates of coating densities. These results serve as preliminary estimates for interpreting the experimental results. Basically, the "average" particle composition is calculated by assuming a spherical kernel and spherical coating shells. The volume and weight fractions were calculated, and then the number of particles per compact was estimated. The fundamental values used in the calculations are listed in Table A-1.

Two reference values were available. The first listed 1.8 g of uranium and 17.69 g of thorium per compact as accountability transfer data; the second listed an ultimate analysis of 8.4% uranium, 80.1% thorium, 11.8% carbon. Since these percentages totaled more than 100, they were adjusted. The thorium value of 17.69 g was taken as the basis from which 1.85 g of uranium and 2.60 g of carbon could be calculated. The calculated estimates are given in Table A-2, column 1.

In the individual experiments, aliquots from the combined middle sieve fractions (+9, +20, +42 mesh) were used. The calculated estimates were adjusted (by weight ratio) for the losses, and the +4-mesh material was used for samples of the starting material. The amounts of carbon (8.10 g), heavy metals,and bead-coating materials (0.64 g, based on 2% breakage) were subtracted to yield a new basis (Table A-2, column 2).

The +9-, +20-, and +42-mesh material was combined and divided into eight fractions by three passes through a simple two-way sample splitter. The amount of each material in each fraction was calculated by the weight ratio on the new basis.

Table A-1. Basic Data for Dragon Compact No. 8232

Kernel	British Data	Used	Coatings	British Data	Used	Component	Theoretical Density (g/cc)	Density Used (g/cc)
U, %	8.4 (1.8 g)	8.36 (1.85 g)	IPYC, μ	25	25	UC_2	11.68	11.68
Th, %	80.1 (17.69 g)	79.90 (17.69 g)	SiC, μ	17	17	ThC_2	9.60	9.60
C, %	11.8	11.74 (2.60 g)	OPYC, μ	57	57	IPYC	-	1.50
Total %	100.3	100.00				SiC	3.17	3.10
Th/U atom ratio	9.31 (9.82)	9.55 (9.56)				OPYC	-	1.90
Theoretical density, g/cc	-	8.974				Graphite	2.26	1.90
Density used	8.39	8.39				Kernel	8.974	8.39
Formula	-	$(U,Th)C_{2.58}$						
Avg. diam, μ	457	350, 457						

Table A-2. Summary Sheet of Starting Fuel Composition of Dragon Compact No. 8232

Component	British Data[d]	Combined Middle Fractions	Archive		Graphite Disintegration		Grind-Leach		Burn-Grind-Leach	
			R1	R2	R3	R6	R5	R7	R4	R8
Measured weight, g	116.93	102.62[b,e]	14.008	15.502	10.376	10.717	14.028	13.034	11.942	13.004
U, g	1.85[a]	1.722	0.235	0.260	0.174	0.180	0.235	0.218	0.200	0.218
Th, g	17.69	16.464	2.247	2.488	1.664	1.719	2.251	2.091	1.916	2.086
"C_2 + G,"[f] g	2.60	2.420	0.330	0.366	0.245	0.253	0.331	0.307	0.282	0.307
IPYC, g	1.45	1.350	0.184	0.204	0.136	0.141	0.184	0.171	0.157	0.171
SiC, g	2.40	2.234	0.305	0.338	0.226	0.233	0.305	0.284	0.260	0.283
OPYC, g	6.44	5.994	0.818	0.906	0.606	0.626	0.819	0.761	0.698	0.759
Wt of total C/P,[g] g	32.43	30.181	4.120	4.560	3.051	3.151	4.126	3.833	3.513	3.824
Graphite matrix, g	84.50[c]	72.436	9.888	10.945	7.323	7.562	9.902	9.199	8.432	9.178

[a]Corrected from original data specification of 1.8 g.

[b]Used average bead breakage of 2.0% during crushing.

[c]By difference.

[d]457-μ kernel, 25-μ IPYC, 17-μ SiC, 57-μ OPYC.

[e]Measured 101.83 before sieving; 102.62 after sieving.

[f]"C_2" is the "carbide" carbon with the heavy metals; "G" refers to the extra graphite in the kernel.

[g]C/P represents the coated particle; "total" refers to the isotropic PYC-coated particle.

11. REFERENCES

1. Chem. Technol. Ann. Progr. Rept. May 31, 1968, ORNL-4272, pp. 56-62.
2. Chem. Technol. Ann. Progr. Rept. May 31, 1967, ORNL-4145, pp. 34-50.
3. Chem. Technol. Ann. Progr. Rept. May 31, 1966, ORNL-3945, pp. 27-33.
4. E. L. Nicholson et al., "Recent Developments in Thorium Fuel Processing," pp. 598-607 in Thorium Fuel Cycle, Proceedings of the Second International Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee, May 3-6, 1966.
5. E. L. Nicholson, L. M. Ferris, and J. T. Roberts, "Burn-Leach Process for Graphite-Base Reactor Fuels Containing Carbon-Coated Carbide or Oxide Particles," pp. 145-65 in Proceedings of the Conference on Fuel Cycles of High-Temperature Gas-Cooled Reactors, Held at Brussels, June 10-11, 1965.
6. J. R. Flanary, J. H. Goode, H. O. G. Witte, and V. C. A. Vaughen, Hot-Cell Evaluation of the Burn-Leach Process, Using Irradiated Graphite-Base HTGR Fuels, ORNL-4120 (in preparation).
7. J. R. Flanary and J. H. Goode, Hot Cell Evaluation of the Grind-Leach Process. I. Irradiated HTGR Candidate Fuels: Pyrocarbon-Coated (Th, U)C_2 Particles Dispersed in Graphite, ORNL-4117 (August 1967).
8. J. H. Goode and J. R. Flanary, Hot Cell Evaluation of the Grind-Leach Process. II. Recovery of Uranium and Thorium from Irradiated Pyrolytic-Carbon-Coated Sol-Gel Thoria-Urania Particles, ORNL-4213 (March 1968).

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