



3 4456 0549535 4

**OAK RIDGE NATIONAL LABORATORY**operated by
UNION CARBIDE CORPORATIONfor the
U.S. ATOMIC ENERGY COMMISSION

ORNL - TM - 688

COPY NO. -

30

DATE - September 20, 1963

**COMBUSTION-DISSOLUTION EXPERIMENTS WITH IRRADIATED GRAPHITE-BASE
REACTOR FUEL CONTAINING CARBON-COATED THORIUM-URANIUM
DICARBIDE PARTICLES**

L. M. Ferris - K. S. Warren - J. W. Ullmann

Technicians: L. A. Byrd, C. T. Thompson

ABSTRACT

Four small pieces of simulated HTGR fuel (from the GAIL-IIIA loop experiment) irradiated to approximately 10,000 Mwd/metric ton (U + Th) were burned in oxygen for 5 hr to determine fission product volatility and dissolubility of the ash. Two of the fuel pieces (C-coated Th-U dicarbide particles dispersed in a graphite matrix; Th/U ratio of about 2.5) were burned at 800°C; the other two at about 1200°C. Essentially no uranium, thorium, zirconium, or rare earths volatilized in any experiment. Greater than 78% of the ruthenium was volatile at 800°C and 97-99% at 1200°C. About 25-35% of the cesium vaporized at 800°C and 67-88% at 1200°C. The ThO₂-U₃O₈ combustion ash from the two 800°C runs was completely dissolved in 7 hr in refluxing 13 M HNO₃--0.04 M HF--0.04 M Al(NO₃)₃; the final solutions were about 0.5 M in Th. The ash from the 1200°C runs was slightly more refractory. In one case complete dissolution was achieved; but, in the other, only 97% was dissolved in the 7-hr period. The remaining 3% dissolved in a second 7-hr digestion with fresh reagent. The results of these preliminary experiments indicate that a Burn-Dissolve process for irradiated graphite-base reactor fuels is chemically feasible.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

CENTRAL RESEARCH LIBRARY
 DOCUMENT COLLECTION
 LIBRARY LOAN COPY
 DO NOT TRANSFER TO ANOTHER PERSON
 If you wish someone else to see this
 document, send in name with document
 and the library will arrange a loan.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

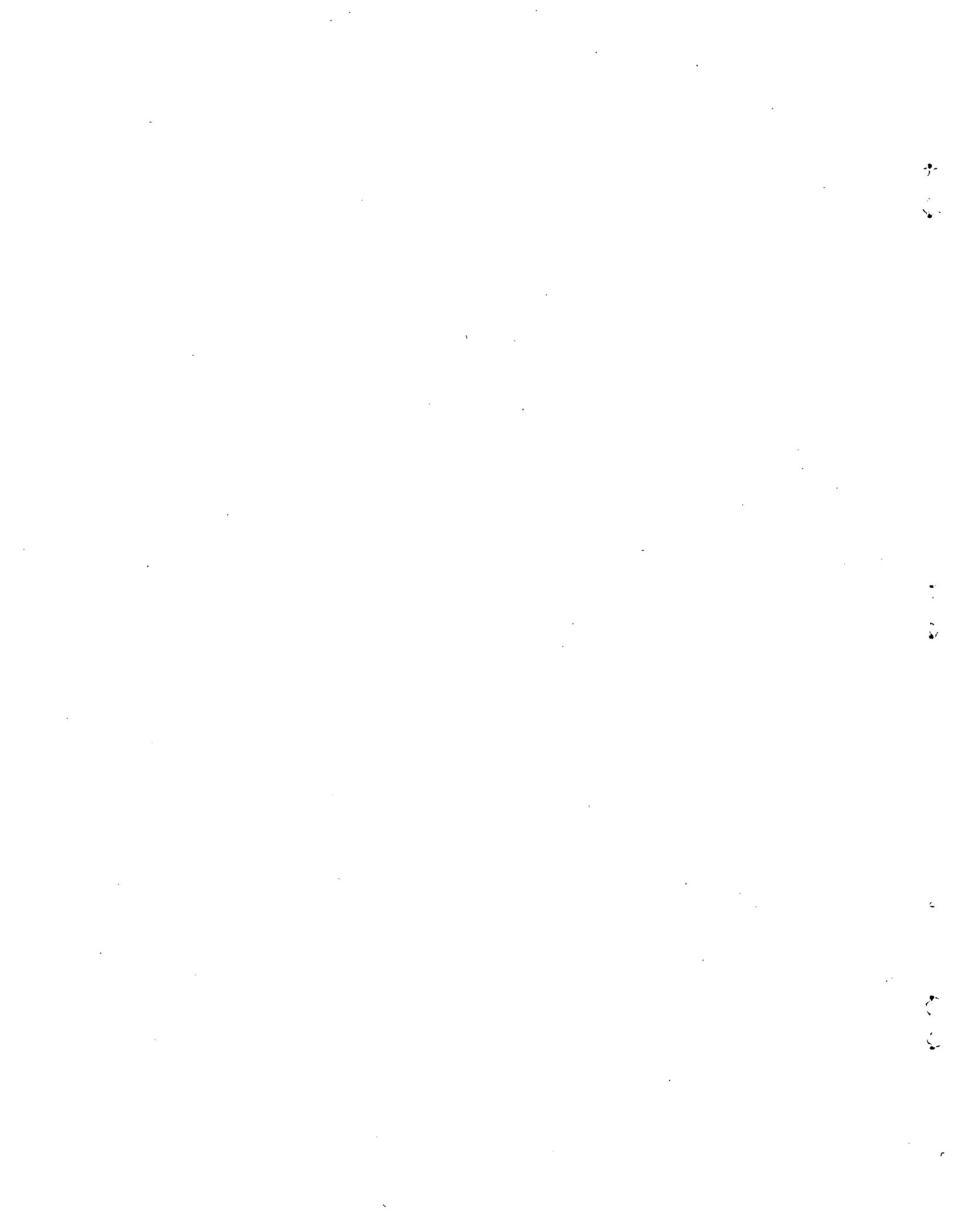
CONTENTS

	Page
Abstract	
1. Introduction	1
2. Equipment and Procedure	2
2.1 Equipment	2
2.2 Procedure	5
3. Results and Discussion	9
3.1 Fuel Burnup and Composition	9
3.2 Fission Product Volatility	10
3.3 Dissolubility of the Combustion Ash	12
4. Recommendations for Future Work	12
5. Acknowledgement	13
6. References	14

OAK RIDGE NATIONAL LABORATORY LIBRARIES



3 4456 0549535 4



1. INTRODUCTION

Over the past several years, ORNL has been studying the problems associated with the processing of graphite-base reactor fuels.¹ Typical examples of graphite-base fuels are those proposed for the Peach Bottom² (HTGR) and AVR³ reactors. The fuel for both of these reactors, although different in both composition and configuration, is essentially a dispersion of carbon-coated U-Th dicarbide particles in the graphite matrix. Based on prior laboratory-scale studies,¹ the most promising head-end method for solvent extraction recovery of uranium and thorium from the coated-particle fuels is combustion in oxygen followed by dissolution of the ash in an aqueous reagent such as fluoride-catalyzed nitric acid.

The purpose of this memo is to summarize the results of four experiments in which small samples of irradiated prototype HTGR fuel were burned in oxygen at high temperature to determine the fate of fission products during combustion and to obtain preliminary data on the effect of combustion temperature on the dissolubility of the $\text{ThO}_2\text{-U}_3\text{O}_8$ ash. Data from these experiments, although preliminary, do allow the prediction of fission product behavior and show that the ash is readily dissolved even when the combustion is conducted at an ambient temperature of 1200°C . Furthermore, these experiments provide a background for more extensive studies with larger and more highly irradiated fuel specimens.⁴

The specimens were from the GAIL-IIIA loop experiment and were provided by General Atomic for the experiments.⁵ The Th/U atom ratio in the specimens was about 2.5, which is lower than expected in actual HTGR or AVR fuel. The burnup of the specimens was quoted⁶ as about 9000 Mwd/metric ton (U + Th), about 1/7 that expected for full-burnup, 75,000 Mwd/metric ton (U^{235} + Th), HTGR fuel.² Two of the specimens were burned at an ambient temperature of 800°C and two at 1200°C , and the extent of fission product volatilization was determined.

2. EQUIPMENT AND PROCEDURE

2.1 Equipment

The combustion experiments were conducted in a quartz reaction vessel heated by a special platinum-wound furnace. A schematic diagram of the entire combustion train is shown as Fig. 1 and a photograph of the actual equipment in the hot-cell is shown as Fig. 2. The combustion tube was a 42-mm-OD, 68-cm-long quartz tube to which a size 65/40 ball joint was connected at the inlet end. A size 18/9 ball joint was sealed to the exit end to allow for connection to the filter unit (Fig. 1). The fuel sample was placed at one end of a section of 38-mm-OD quartz tubing which had the exit end partially sealed off. This tube served as the reaction boat and was just long enough to position the sample at the center of the furnace when it was inserted into the combustion tube so that its inlet end was flush with the inlet end of the combustion tube (Fig. 1). The large ball joint on the inlet end was affixed with connections for admitting oxygen or applying a vacuum.

The resistance furnace, with which temperatures of 1400°C were readily attained, consisted of an ungrooved 1.5-in.-dia alundum tube (Norton Mixture RA 98) wound with 70 ft of #20 alloy wire (80% Pt-20% Rh) which was held in place with Norton RA 1098 refractory cement and insulated with Carborundum Fiberfrax. A Pt-Pt/10% Rh thermocouple was imbedded in the cement adjacent to the alundum core, and connected to a Barber-Colman Wheelco Model 402 Capacitrol with associated relays for temperature control. The entire furnace was mounted on two bearings in line with the center and perpendicular to the furnace axis so that it could be rotated by a 1-rpm reversible motor in either direction from the normal level position.

The filter unit (ORNL drawing D-57500) contained both a porous nickel and a millipore paper disk filter (Fig. 1). Porous nickel (about 40 μ) disks were machined out of grade E sheet stock obtained from the Micro Metallic Division of the Pall Corporation, 30 Sea Cliff Avenue, Glen Cove, New York. These nickel disks were then cemented into the center of aluminum flanges which were machined to give a tight fit. Epoxy resin was applied to the edge of the nickel, thus ensuring that all gaseous combus-

UNCLASSIFIED
ORNL DWG. 63-4890

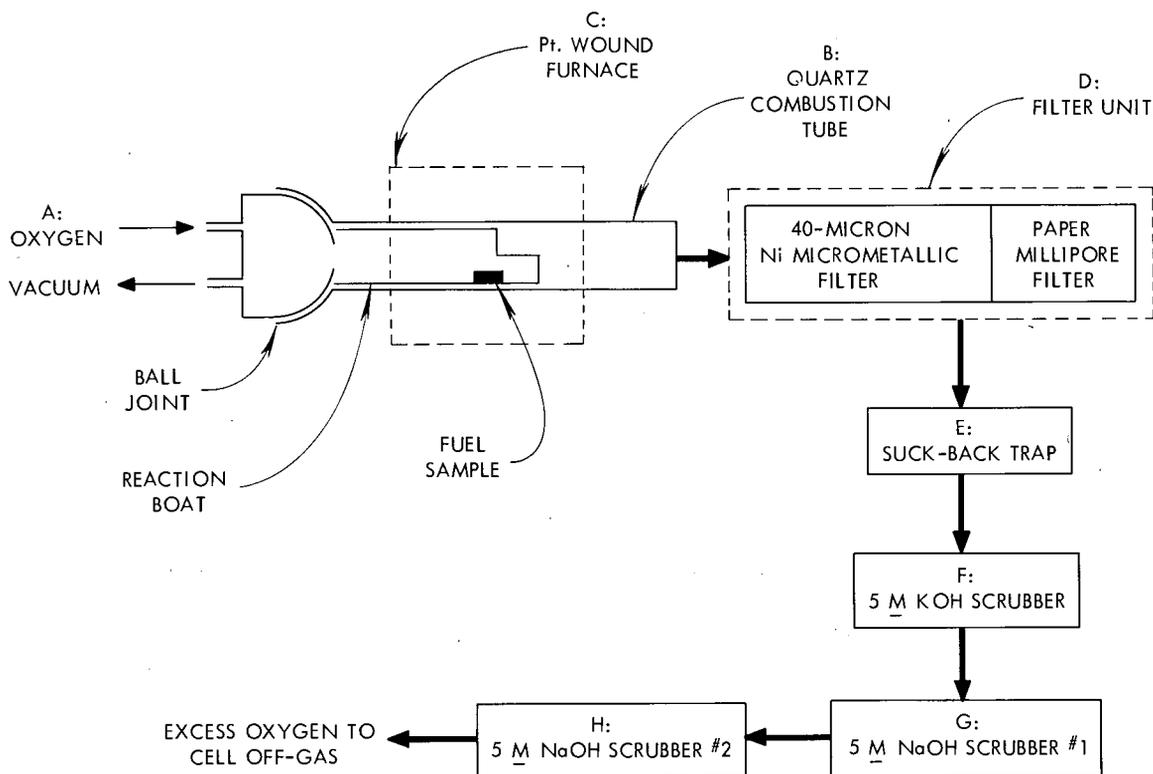


Fig. 1. Schematic Diagram of Combustion Train Used in Experiments with Irradiated HTGR Fuel.

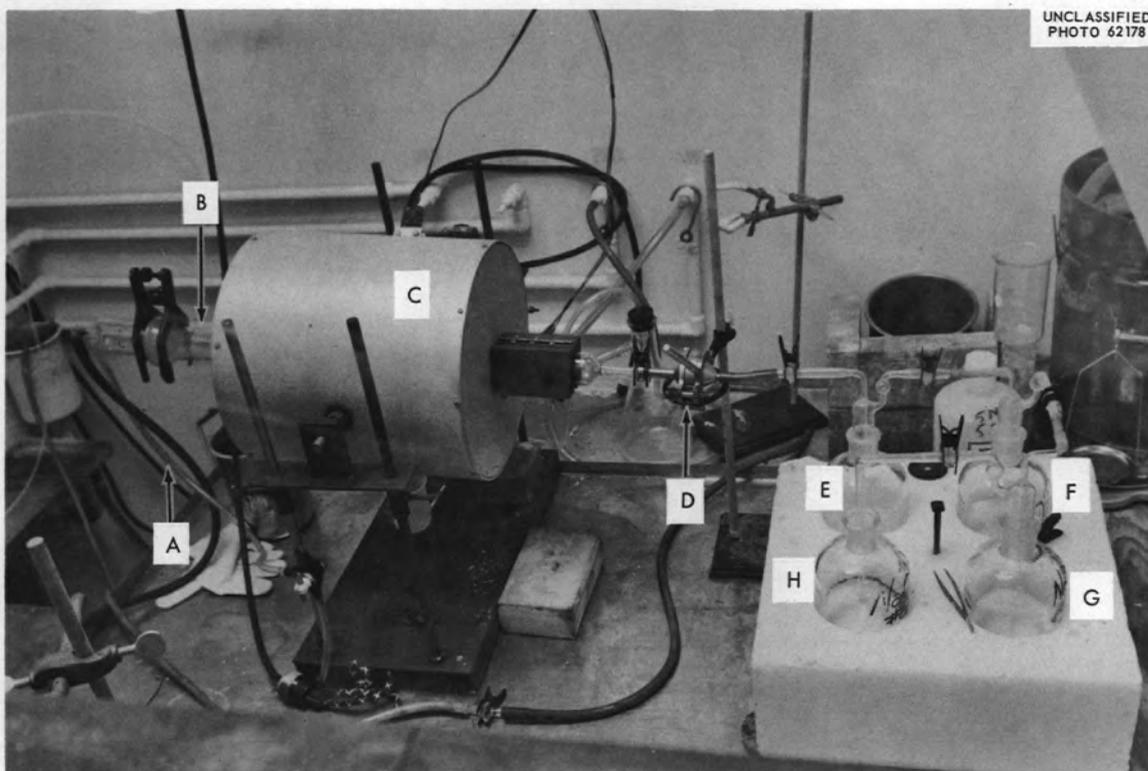


Fig. 2. Photograph of Equipment Used in the Combustion of Irradiated HTGR Fuel Samples. A: oxygen inlet tube; B: reaction vessel; C: platinum-wound furnace; D: filter unit; E: suck-back trap; F: KOH scrubber; G: NaOH scrubber number 1; H: NaOH scrubber number 2.

tion products were filtered through the full thickness of the porous nickel. A picture of a completed nickel filter is shown in Fig. 3. The paper filter disks (Catalog No. SMWP 047 00, Millipore Filter Corporation, Bedford, Mass.) had an average porosity of 5μ but had been shown by experience^{7,8} to retain almost all particles with diameters greater than 1μ . The stainless steel filter unit (which was maintained at room temperature) consisted of three flanges hinged together at one junction (Fig. 3); a wing nut diametrically opposite the hinge was used to secure the filters between the flanges. Neoprene gaskets were used to hold the filters in place. A photograph of the filter unit after the wing nut was partially tightened is shown as Fig. 4.

The filter unit was connected to the first of a series of scrubber bottles by a ball joint. The scrubber bottles, each of 1-liter capacity, were also connected to one another by ball joints (Fig. 2). The first bottle was empty and served as a suck-back trap. The next bottle contained 500 ml of 5 N KOH, while the last two bottles each contained 500 ml of 5 N NaOH.

2.2 Procedure

At the beginning of each experiment a piece of HTGR fuel (containing about 1 g of U + Th) was placed in one end of the reaction boat. The boat was then slid into the combustion tube to position the fuel sample in the center of the furnace. After connection of all the components of the combustion train, oxygen was admitted to the system at a rate of 960 cc/min, the rate being measured at 25°C. The furnace was then brought slowly to the desired ambient temperature (the temperature measured by the thermocouple imbedded near the heating element). Although the fuel samples did not ignite until an ambient temperature of about 600°C was reached, most of the graphite matrix was probably burned during the heating period since at least 6 hr of heating was required to attain even the lowest ambient temperature, 800°C. Nevertheless, the system was maintained at temperature for 6 hr once it was reached. After maintaining the system at the ambient temperature for 6 hr, the furnace was cooled to room temperature; then, the boat was removed from the combustion

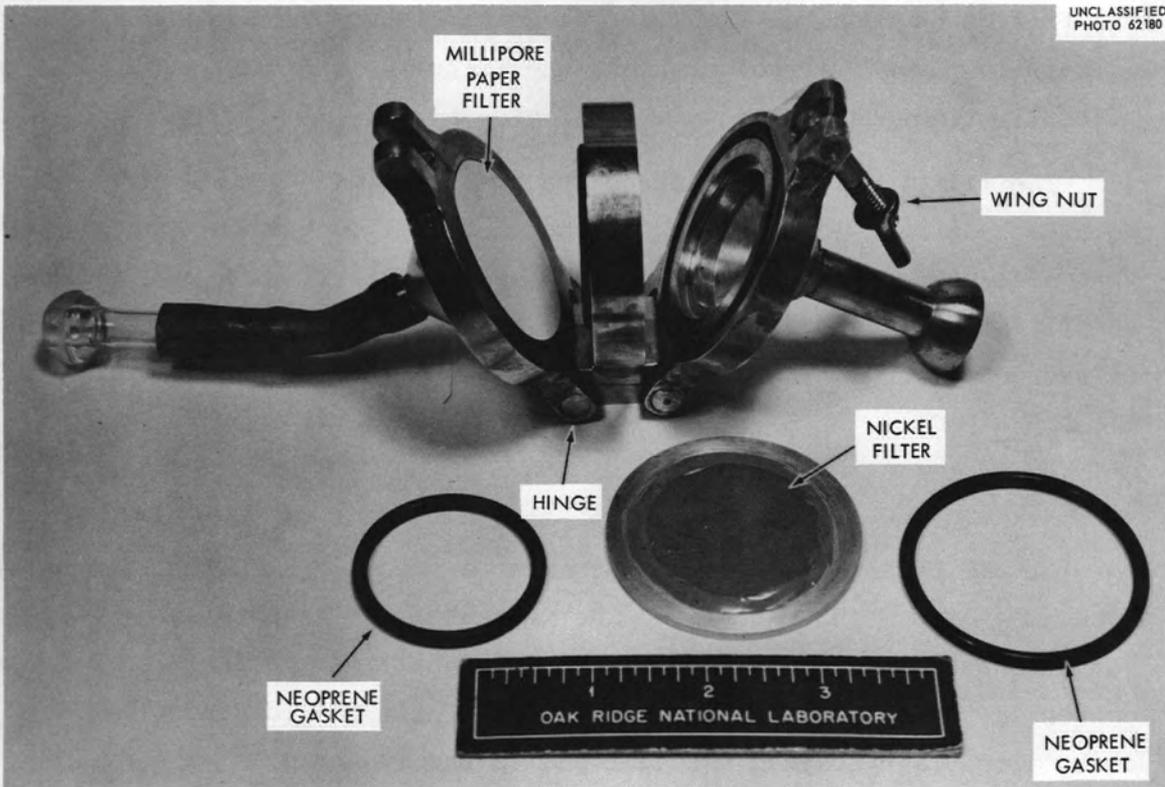


Fig. 3. Open View of Filter Unit and Component Parts.

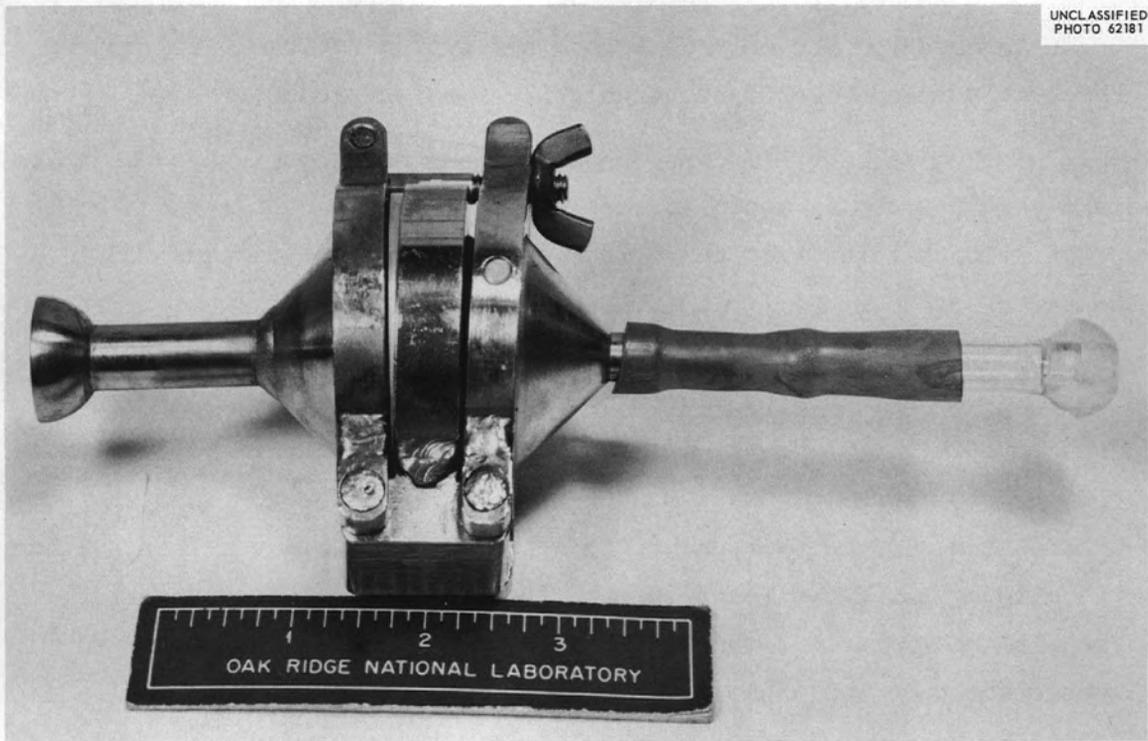


Fig. 4. Filter Unit After Closure and Nearly Complete Tightening of the Wing Nut.

tube and its contents (the $\text{ThO}_2\text{-U}_3\text{O}_8$ ash) were transferred to a dissolver. The ash was digested for 7 hr in sufficient refluxing 13 M HNO_3 --0.04 M HF --0.04 M $\text{Al}(\text{NO}_3)_3$ to produce a solution containing about 0.5 M Th if all the ash dissolved. If the ash was not dissolved during the first 7-hr digestion, the residue was refluxed for 7 more hr in the same volume of fresh reagent. The solutions obtained from the ash dissolution were analyzed for uranium, thorium, and fission products. The reaction boat was washed with hot 6 M HNO_3 --0.02 M HF and the resulting solution analyzed. Fission products found in the solutions obtained from ash dissolution and washing the boat were considered as nonvolatile fission products.

Fission products condensed on the inner surface of the combustion tube were removed as two different samples. First, the furnace was rotated so that the exit end of the combustion tube was immersed in a beaker of hot 6 M HNO_3 --0.02 M HF . Vacuum was applied from the inlet end of the tube and 60 to 80 ml of the acid was sucked into the tube tip. The acid was agitated by vacuum in the tube tip for about 15 minutes. The resulting solution was then analyzed. After leaching of the tube tip, 500 to 700 ml of hot 6 M HNO_3 --0.02 M HF was sucked into the combustion tube to wash virtually the entire inner surface. This solution was also agitated for about 15 min; it was then analyzed separately. The fission products found in the solutions obtained by washing the combustion tube and those collected on the filters and in the alkali scrubbers were considered to be volatile fission products.

The metal and paper filters were transferred directly to a "hot" analytical laboratory for dissolution and analysis. Aliquots of the caustic scrubber solutions were taken for analysis.

Virtually no radioactive species passed through the combustion train into the interior of the hot cell. Excess oxygen, of course, transited the system and ultimately entered the cell off-gas system. Preliminary tests showed that in a typical combustion experiment, about 90% of the CO_2 was sorbed in the first scrubber (KOH) and practically all the remainder was sorbed by the second scrubber (NaOH).

3. RESULTS AND DISCUSSION

3.1 Fuel Burnup and Composition

The burnup and composition of the fuel specimens were computed in two ways: (1) using the cesium analyses and the amounts of uranium and thorium determined by direct chemical analyses of the various samples, and (2) using the cesium analyses and the weight of combustion ash assuming a Th/U weight ratio of 2.5. Use of the second method was prompted by the fact that the ash weights obtained were much greater than those expected from the amounts of uranium and thorium found (Table 1), although the Th/U ratio was essentially that expected in the fuel.⁵ The explanation for this discrepancy may be difficulties in the uranium and thorium analyses. The burnups calculated by the two methods varied from 4700 to 12,400 Mwd/metric ton (U + Th), but the average value obtained by each method was within 20% of the average burnup of 8850 Mwd/metric ton (U + Th) quoted by General Atomics^{5,6} (Table 2).

Although the calculated burnups vary considerably, the data on the volatility of the fission products should not be affected in a qualitative sense.

Table 1. Comparison of Actual Ash Weights with Those Computed from Total Uranium and Thorium Found by Analysis

Run No.	Th/U Wt. Ratio	Wts of Oxides Calc. From U and Th Analyses(g)		Ash Weight (g)	
		U_3O_8	ThO_2	Actually Found	Calculated From Uranium and Thorium Analyses
1H	2.6	0.154	0.390	0.67	0.544
2H	2.7	0.118	0.310	0.78	0.428
3H	2.4	0.200	0.458	0.90	0.658
4H	2.3	0.229	0.508	0.99	0.737

Table 2. Comparison of Sample Burnups and Compositions Calculated From Actual Uranium and Thorium Analyses and From Weight of Combustion Ash Assuming a Th/U Weight Ratio of 2.5

Run No.	U in Sample (%)		Th in Sample (%)		Burnup [Mwd/metric ton (U + Th)]	
	From Chemical Analyses	From Ash Weight	From Chemical Analyses	From Ash Weight	From Chem. Analyses	From Ash Weight
1H	7.70	9.88	20.2	24.7	12300	9900
2H	4.17	8.12	11.3	20.3	8600	4700
3H	5.86	7.76	13.9	19.4	12400	4800
4H	<u>5.70</u>	<u>7.29</u>	<u>13.1</u>	<u>18.2</u>	<u>8900</u>	<u>9200</u>
Avg:	5.86	8.26	14.6	20.6	10000	7150
GA Spec. (ref. 5)	6.8		16		8850	

3.2 Fission Product Volatility

As expected, appreciable quantities of ruthenium and cesium were volatilized during the combustion. Although the data were not consistent at each temperature, perhaps due to incomplete washing of the tube and tube tip, it was shown that more than 78% of the ruthenium volatilized at an ambient temperature of 800°C, while at 1200°C its volatilization was 97-99% (Table 3). Cesium was somewhat less volatile; 25-35% vaporized at 800°C and 67-88% volatilized at 1200°C. Very little zirconium or rare earths were found outside the reaction boat (Table 3). These results, along with analyses for uranium, thorium, and gross alpha activity, show also that little entrainment of ash particles occurred under the conditions used.

Just as the total amounts of ruthenium and cesium volatilized were different in what should have been identical experiments, their distribution within the combustion train varied with each run (Table 4). For example, in the two runs at 1200°C (runs 3H and 4H), 80% of the ruthenium was found at the tube tip in one case but only 10% in the other. Although the amounts of ruthenium and cesium reaching the 40-μ-porosity filter

Table 3. Amounts of Fission Products Volatilized During Combustion of HTGR Fuel Samples

Run No.	Temp. (°C)	Amount of Fission Product Volatilized (%)			
		Ru	Cs	Zr	TRE
1H	800	78	24	0.008	0.02
2H	800	96	35	0.07	0.1
3H	1200	97	67	0.04	0.06
4H	1200	99	88	0.02	0.01

Table 4. Distribution of Ruthenium and Cesium in the Combustion Train

Sample	Amount Found in Run (%)							
	1H		2H		3H		4H	
	Ru	Cs	Ru	Cs	Ru	Cs	Ru	Cs
Ash	22.3	75.9	3.6	64.7	2.9	32.9	0.6	12.2
Tube	58.2	14.0	23.6	0.4	10.4	1.6	2.1	2.0
Tube tip	6.6	9.4	46.4	17.5	79.2	60.2	10.1	59.5
Metal filter	12.9	0.8	26.0	17.3	7.3	5.1	65.8	26.1
Paper filter	0.01	0.008	0.007	0.003	0.04	0.14	21.5	0.19

varied from run to run, generally very little passed through to the paper filter. Only in run 4H was there a significant (22%) amount of ruthenium caught on the paper filter. Gross beta and gross gamma analyses of the scrubber solutions were generally below the limit of detection, showing that almost no activity passed through the filter unit. The decontamination factors across the filter unit calculated on the basis of gross beta and gross gamma activities were at least 10^4 .

The results obtained in this study are in general agreement with those of a previous similar investigation¹ in which low-burnup (about 0.001%) graphite fuel specimens containing uranium dicarbide were burned in oxygen at about 900°C for 3 hr. In the prior study, between 40 and 95% of the

ruthenium was volatilized; however, no cesium volatilization was detected. The nonvolatility of cesium in the earlier experiments cannot be explained on the basis of different gas flow rates since the linear gas velocities were about the same as those in the present study. The only apparent explanation is that the reaction periods were much shorter in the earlier series of experiments. As in the present study, the previous work showed zirconium and cerium to be nonvolatile.

The results of the present study are also in qualitative agreement with those obtained in the in-pile combustion of uranium carbide--graphite fuel pieces.⁹ The fuel pieces, which contained carbon-coated uranium di-carbide particles, were burned in air in the Oak Ridge Research Reactor for 15 min; the combustion temperature reached 1400°C. Little or no strontium, zirconium, barium, cerium, or uranium were volatilized; however, 35-40% of the cesium and 5 to 40% of the ruthenium were volatile.

3.3 Dissolubility of the Combustion Ash

One of the primary objectives of this study was to determine, in a cursory manner, the effect of combustion temperature on the dissolubility of the $\text{ThO}_2\text{-U}_3\text{O}_8$ ash. In each experiment, the ash was a relatively free-flowing powder, easily poured from the reaction boat. The ash from each run was digested for 7 hr. in sufficient boiling 13 M HNO_3 --0.04 M HF --0.04 M $\text{Al}(\text{NO}_3)_3$ to produce a solution that was 0.5 M in Th if all the ash dissolved. Only the ash from run 3H was not completely dissolved under these conditions. About 97% dissolved during the first 7-hr digestion; the remainder dissolved during an additional 7-hr digestion with the same volume of fresh dissolvent. These results indicate that combustion at relatively low temperatures (less than 1200°C) of graphite fuels containing thorium would produce an ash that not only could be easily removed from the burner but also would dissolve readily in the conventional dissolvent for thorium and ThO_2 .

4. RECOMMENDATIONS FOR FUTURE WORK

The results of the preliminary combustion experiments reported in this memo lead to many suggestions for further study, perhaps in connection

with the anticipated graphite-fuel campaign in high-level cells⁴. These suggestions are itemized below:

1. More development of the analytical methods used is indicated so that fuel compositions and burnups can be determined with a higher degree of confidence.
2. Studies of the effect of combustion conditions on the volatility of fission products should be extended emphasizing the following factors:
 - (a) Fuel composition - for example the effects of other potential fuel components such as SiC and variations in the Th/U ratio on the retention of fission products by the ash.
 - (b) Fuel burnup.
 - (c) Oxidizing-gas composition (e.g. N_2-O_2 mixtures) and flow rate (actually, the effect of rate of combustion) should be studied. In connection with studies of this sort, perhaps the fuel specimen should be heated to temperature in an inert gas before the oxidizing gas is admitted.
 - (d) Reaction time.
3. The solubility of the combustion ash from very high burnup fuels has never been tested. Rates of dissolution and stability of solutions with high fission product contents need to be determined.
4. In connection with the dissolution of ash from high burnup fuel, studies of the solvent extraction behavior should be made.
5. Methods for removing the fission products from the combustion system and storing them should be considered.

5. ACKNOWLEDGEMENT

The authors thank J. R. Flanary and J. H. Goode, ORNL Chemical Technology Division, for their helpful suggestions for designing the combustion equipment. We also thank K. G. Steyer and H. E. Shoemaker of General Atomic for their cooperation in supplying the irradiated fuel samples. Chemical and radiochemical analyses were provided by the groups of C. E. Lamb and E. I. Wyatt, ORNL Analytical Chemistry Division.

6. REFERENCES

1. L. M. Ferris, A. H. Kibbey, and M. J. Bradley, Processes for Recovery of Uranium and Thorium from Graphite-Base Fuel Elements, Part II, ORNL-3186 (November 16, 1961).
2. W. V. Goedel, ed., Pyrolytic-Carbon-Coated Carbide Fuel Particles and Their Use in Graphite-Matrix Fuel Compacts, GA-3588 (Oct. 30, 1962).
3. A. W. Savolainen, ed., Gas-Cooled Reactor Semi-annual Progress Report for Period Ending September 30, 1963, ORNL-3523 (in preparation).
4. Letter, J. R. Flanary, ORNL, to R. E. Blanco, ORNL, Revised PRFP Hot Cell Schedule - FY 1964-1965 (September 4, 1963).
5. Quarterly Progress Report for the Period Ending June 30, 1962. 40-MW(E) Prototype High-Temperature Gas-Cooled Reactor, GA-3396 (June 30, 1963).
6. Letter, K. G. Steyer, General Atomic, to J. W. Ullmann, ORNL, January 30, 1963.
7. Personal communication, W. J. Martin, ORNL, to K. S. Warren, ORNL, September 16, 1963.
8. G. W. Parker, G. W. Creek, and W. J. Martin, Fission Product Release from UO_2 by High Temperature Diffusion and Melting in Helium and Air, ORNL-CF-60-12-14 (February 14, 1961).
9. ORNL Status and Progress Report, March 1963, ORNL-3436 (April 8, 1963).

DISTRIBUTION

Internal

- | | |
|---------------------------|--------------------------------|
| 1. R. E. Blanco | 19. L. E. McNeese |
| 2. J. C. Bresee | 20. E. L. Nicholson |
| 3. R. E. Brooksbank | 21. A. D. Ryon |
| 4. K. B. Brown | 22. W. F. Schaffer |
| 5. G. I. Cathers | 23. C. D. Scott |
| 6. F. L. Culler | 24. J. W. Ullmann |
| 7. B. C. Deering, AEC, OR | 25. K. S. Warren |
| 8. D. E. Ferguson | 26. C. D. Watson |
| 9. L. M. Ferris | 27. M. E. Whatley |
| 10. B. C. Finney | 28. H. B. Whetsel |
| 11. J. R. Flanary | 29. R. G. Wymer |
| 12. H. E. Goeller | 30-31. C R Library |
| 13. J. H. Goode | 32. Document Reference Section |
| 14. W. O. Harms | 33-34. Laboratory Records |
| 15. B. A. Hannaford | 35. Laboratory Records-RC |
| 16. R. W. Horton | |
| 17. A. I. Irvine | |
| 18. F. G. Kitts | |

External

36. E. L. Anderson, Jr., AEC, Wash.
37. R. D. Baker, LASL
38. L. C. Corrington, SNPO (Cleveland)
39. D. C. Davis, ORO
40. L. P. Hatch, BNL
41. S. A. Larowski, ANL
42. G. B. Marrow, Y-12
43. A. R. Matheson, General Atomics
44. J. A. McBride, ICPP
45. P. D. Miller, BMI
46. J. W. Morris, SRL
47. R. E. Pahler, AEC, Wash.
48. W. H. Reas, HAPO
49. W. S. Scheib, AEC, Wash.
50. J. L. Schwennesen, AEC, Wash.
51. C. M. Slansky, ICPP
52. S. H. Smiley, ORGDP
53. G. Strickland, BNL
- 54-68. DTIE
69. R and D Division, ORO
70. B. Vondra, NUMEC