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COMBUSTION-DISSOLUTION EXPERIMENTS WITH IRRADIATED ROVER (KIWI-B4A) FUEL

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CONTENTS

Page

Abstract

1. Introduction 1

2. Equipment and Procedure 1

2.1 Equipment 1
2.2 Procedure 7

3. Results 8

3.1 Fuel Burnup and Composition 8
3.2 Fission Product Volatility 10
3.3 Dissolubility of the Combustion Ash 10

4. Discussion 11

5. Acknowledgement 13

6. References 14

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ABSTRACT

Fuel element specimens from the Kiwi-B4A reactor, which were lined with NbC but which did not contain coated fuel particles, were burned for 6 hr in oxygen at ambient temperatures ranging from 700 to 1400°C to determine fission product volatility and dissolubility of the U_3O_8-Nb_2O_5 ash in HF-HNO_3 solution. Uranium, niobium, zirconium, cerium, and strontium were virtually nonvolatile during combustion. Ruthenium and cesium were volatilized to a considerable extent, especially at 1200 and 1400°C. The amount of ruthenium volatilized increased from 35% to nearly 100% as the ambient temperature increased from 700 to 1400°C. Little cesium volatility was noted at 700°C, but, at 1400°C, as much as 40% volatilized. Essentially none of the volatile activity passed through a 40-μ porosity nickel filter maintained either at room temperature or at 200°C.

In each experiment, the U_3O_8-Nb_2O_5 ash was very friable and dissolved completely in 7 hr in boiling 5 M HF--5 M HNO_3 (F/Nb mole ratios of 70 to 80).

The results of these experiments indicate that a Burn-Dissolve process for Rover fuels is chemically feasible if the combustion temperature is controlled to 1400°C or lower.

1. INTRODUCTION

Oak Ridge National Laboratory is developing Aqueous,[1-3] Fluoride Volatility,[4-6] and Chloride Volatility[7,8] processes for recovering uranium from Rover fuel elements. Each method involves combustion of the fuel, in oxygen or air-oxygen mixtures, at one stage of the process. Obviously, the fate of fission products during combustion is of vital concern to each of the processes being considered. In this connection, several irradiated Rover fuel specimens (actually, from the Kiwi-B4A test) were burned in oxygen at ambient temperatures of 700 to 1400°C primarily to determine fission product volatility and also to evaluate cursorily the dissolubility of the U_3O_8-Nb_2O_5 ash in HF-HNO_3 solution. The fuel specimens, which were lined with NbC but did not contain coated (or "beaded") fuel particles, were used for these tests since no coated particle fuel was available. The results of these experiments are reported in this memo.

2. EQUIPMENT AND PROCEDURE

2.1 Equipment

Combustions were conducted in quartz reaction vessels which were 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 vacuum.

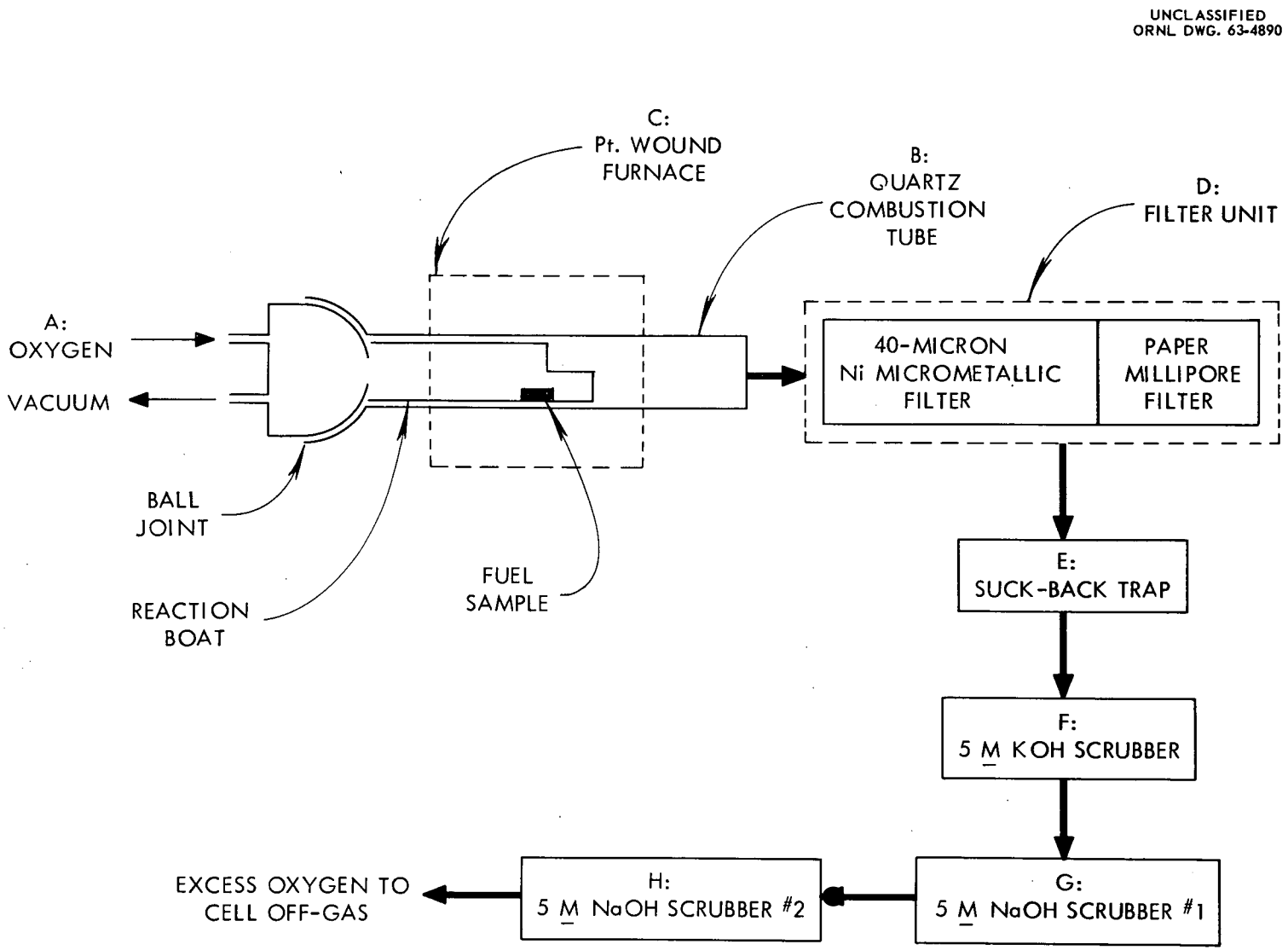

Fig. 1. Schematic Diagram of Combustion Train Used in Experiments with Irradiated Rover Fuel.

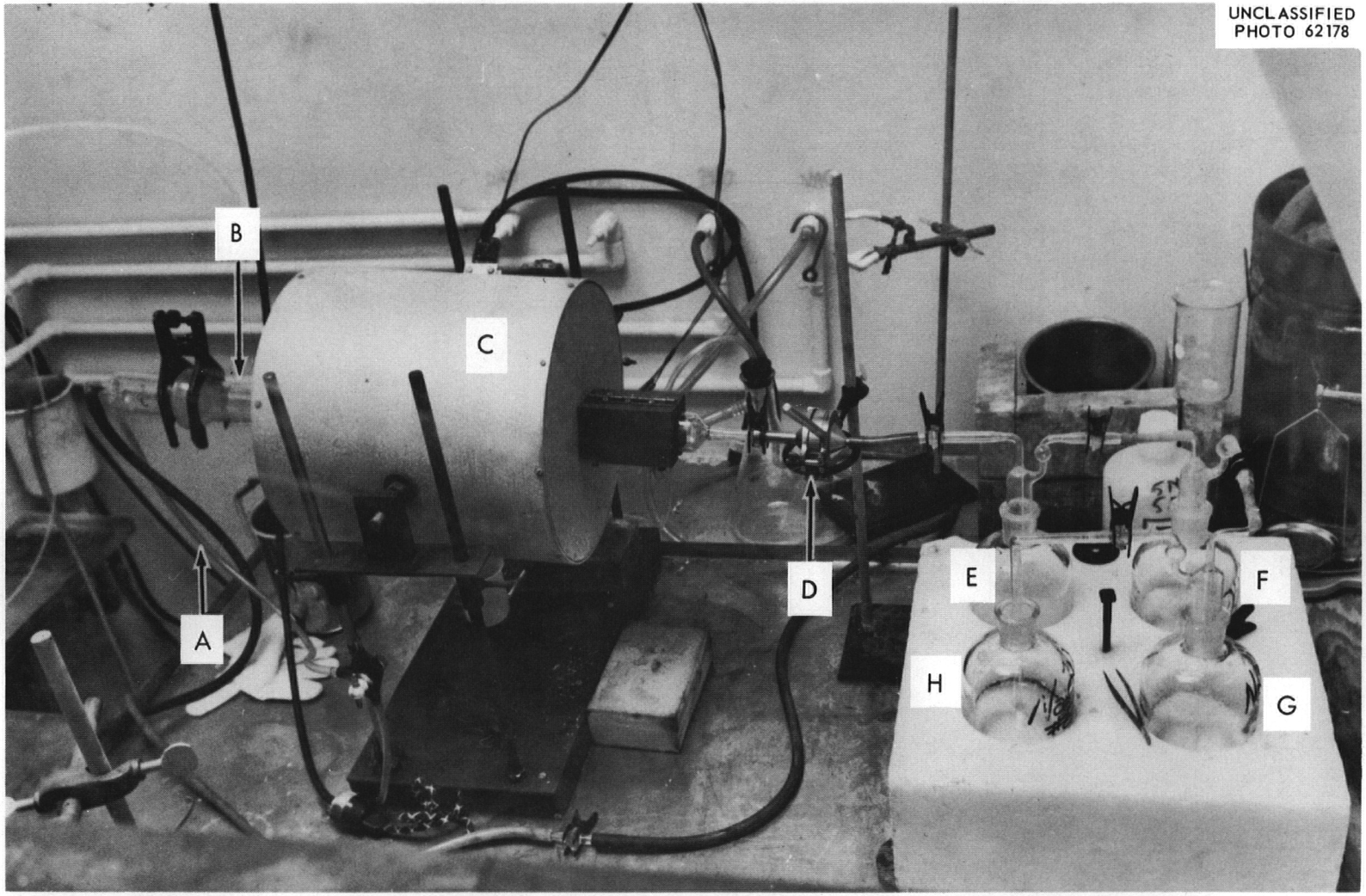

Fig. 2. Photograph of Equipment Used in the Combustion of Irradiated Rover Fuel Samples. A: Oxygen inlet tube; B: Reaction vessel; C: Pt-wound furnace; D: Filter unit; E: Suck-back trap; F: KOH scrubber; G: NaOH scrubber No. 1; H: NaOH scrubber No. 2.

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 No. D-57500) contained both a porous nickel and Millipore paper disk filter (Fig. 1). Porous nickel (about 40-μ pores) 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. The epoxy resin used as cement was applied to the edge of the nickel, thus ensuring that all gaseous combustion products were filtered through the full thickness of the filter. 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, Massachusetts) had an average porosity of 5 μ but had been shown by experience[9,10] to retain almost all particles with diameters greater than 1 μ. The stainless steel filter unit 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 when the unit was maintained at room temperature; Teflon O-rings were used as gaskets when the unit was at 200°C. 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.

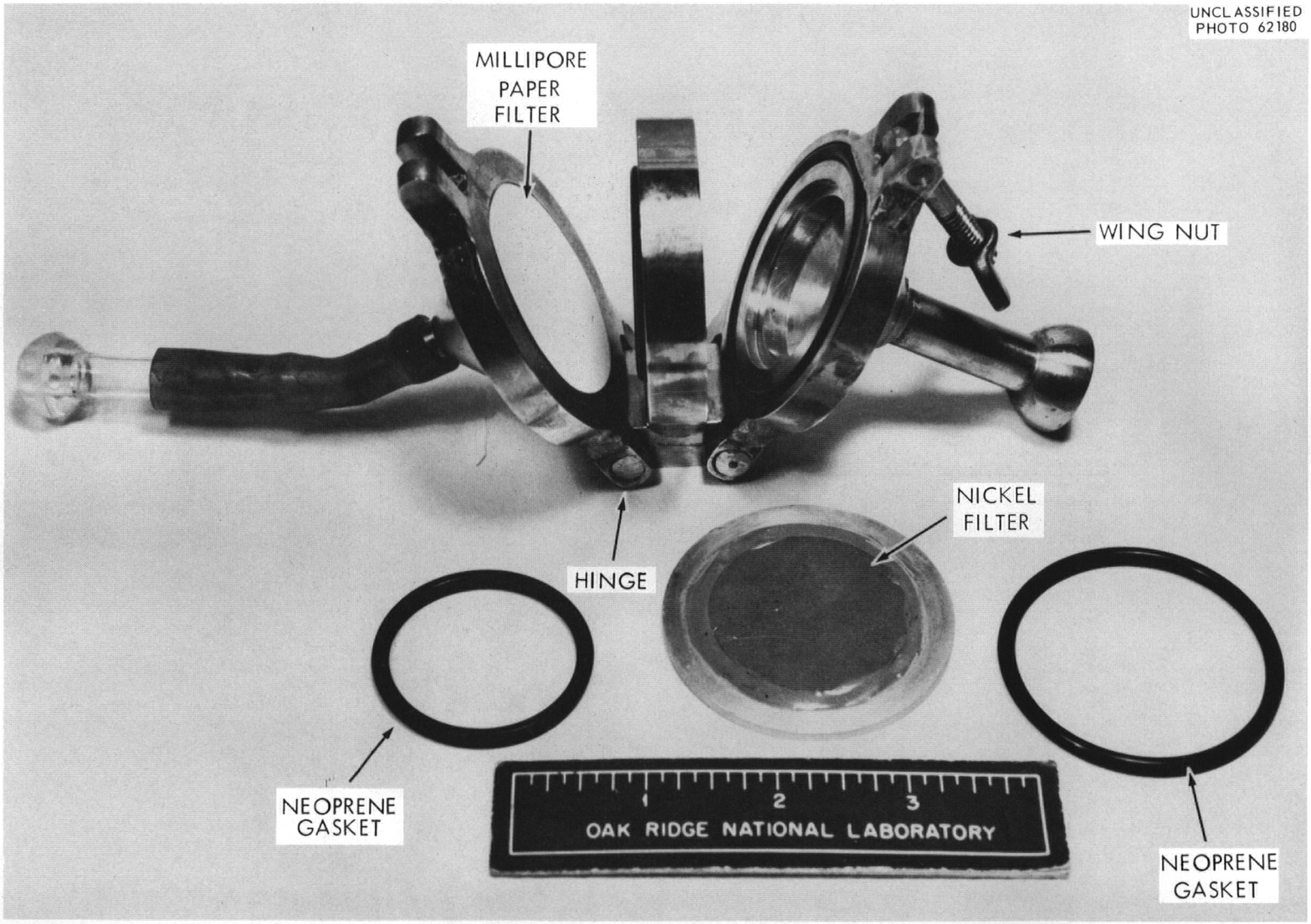

Fig. 3. Open View of Filter Unit and Component Parts.

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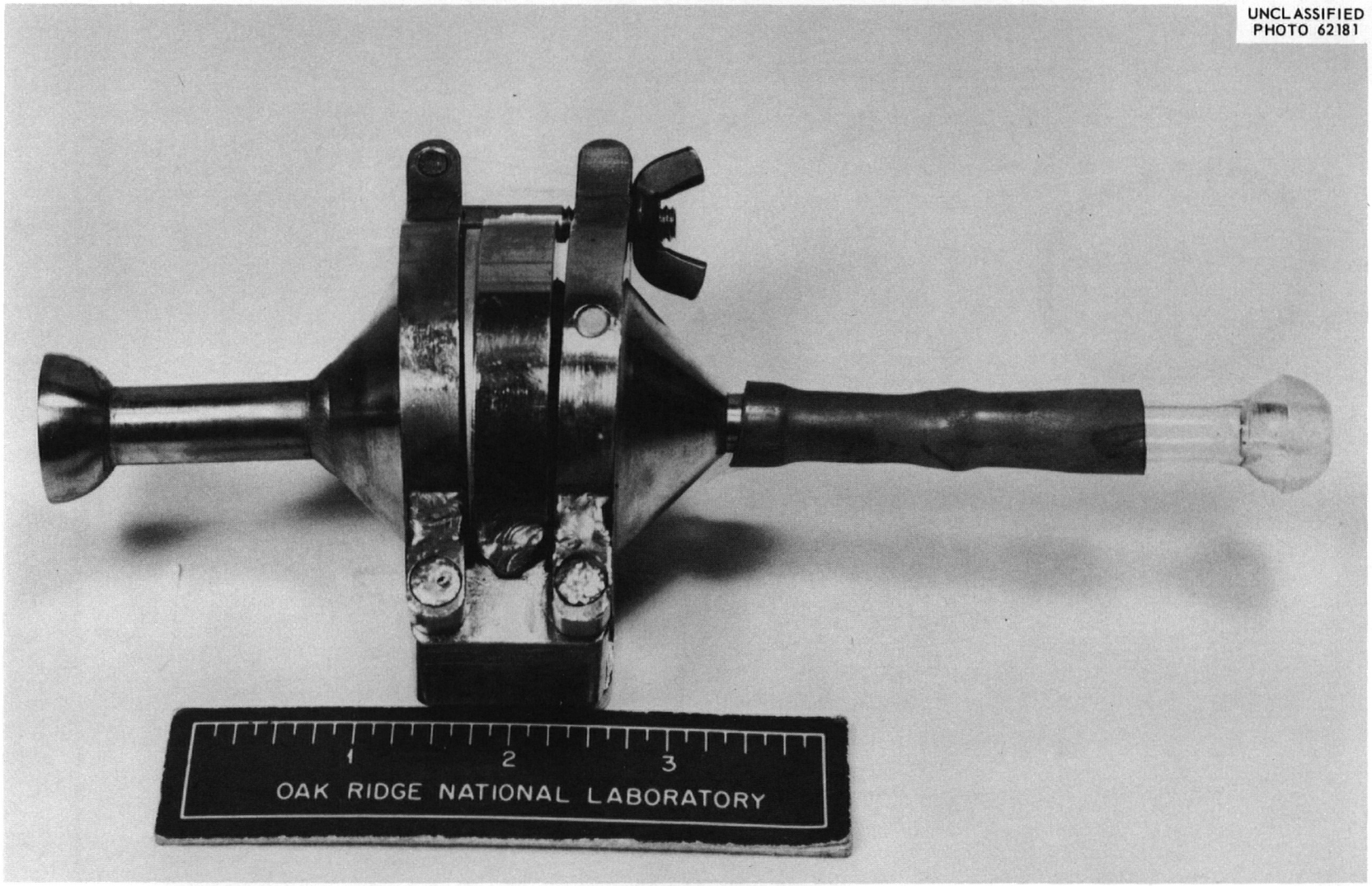

Fig. 4. Filter Unit After Closure and Nearly Complete Tightening of the Wing Nut.

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2.2 Procedure

At the beginning of each experiment, a 1-in. length of Rover fuel (weighing from 9 to 13 g) 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 5 hr of heating was required to attain the lowest ambient temperature, 700°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 tube and its contents (the U_3O_8-Nb_2O_5 ash) were transferred to a Teflon dissolver. The construction of this dissolver has been described previously.[3] The ash was digested for 7 hr in refluxing 5 M HF--5 M HNO_3 (F/Nb mole ratio of 70 to 80). The solutions obtained from the ash dissolutions were analyzed for uranium, niobium, and fission products. The reaction boat was washed with hot 6 M HNO_3--0.02 M HF and the resulting solution analysed. 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 for about 15 min in the tube tip; then, the resulting solution was removed for analysis. 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 15 min; then, it was 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 analysis. Aliquots of the 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).

Eight experiments were conducted between 700 and 1400°C with the filter unit at room temperature. In addition, 700°- and 1400°-runs were made with the filter unit held at about 200°C. A paper filter could not be used when the filter unit was maintained at 200°C.

3. RESULTS

3.1 Fuel Burnup and Composition

The burnup was calculated from the uranium and cesium analyses; the composition from the uranium and niobium analyses. The average burnup, 1.4 Mwd/metric ton of uranium (Table 1), is slightly lower than the range of 2 to 6 Mwd/metric ton calculated from data given by LASL.[11] However, since the position in the reactor of the fuel pieces used in the combustion studies was not specified, the burnup data can be considered in general agreement. The uranium (average of 15.5%) and niobium (average of 9.69%) contents (Table 1) of the fuel are about those expected from work with similar unirradiated fuel specimens.[2,3] Furthermore, generally good agreement among actual ash weights and those calculated from the uranium and niobium analyses was obtained (Table 2).

Table 1. Burnup and Composition of KIWI-B4A Fuel Specimens Used in Combustion Experiments

Run	Fuel Composition (%) Uranium	Fuel Composition (%) Niobium	Burnup (Mwd/metric ton Uranium)
1	14.2	---	2.6
2	16.5	9.86	1.9
3	13.2	8.98	0.81
4	22.1	9.72	0.88
5	16.3	10.1	1.6
6	16.8	10.4	1.8
7	14.0	9.25	0.86
8	16.9	9.43	1.1
9	12.7	9.76	1.1
10	12.1	9.72	1.3
Avg.	15.5	9.69	1.4

Table 2. Comparison of Actual Ash Weights with Those Computed from Uranium and Niobium Analyses

Run	Sample Wt (g)	Wt of Ash (g) Found	Wt of Ash (g) Calculated	Wt Balance (%) (Wt found/wt calc.) x 100
1	12.8	4.39	--	--
2	13.2	4.46	4.43	99
3	14.5	5.0	4.11	82
4	12.3	4.19	4.93	118
5	12.9	4.44	4.34	98
6	12.6	4.35	4.35	100
7	9.94	3.42	2.96	86
8	13.2	4.48	4.43	99
9	12.3	3.94	3.56	90
10	12.8	4.41	3.63	82

3.2 Fission Product Volatility

As expected, appreciable amounts of both ruthenium and cesium volatilized during the combustion. Although the data were not consistent at each temperature, especially those for cesium, it was shown that the amounts volatilized increased with increasing temperature. Specifically, the amount of ruthenium volatilized increased from a low of 35% to almost 100% as the temperature was increased from 700 to 1400°C (Table 3). The results for cesium, although erratic, indicated little volatility at 700°C, with up to 40% volatilization at 1400°C (Table 3). Virtually no zirconium, cerium, or strontium was detected outside the reaction boat. These results, along with those for uranium, niobium, and gross alpha activity, show that little if any entrainment of the oxide ash occurred under the conditions used.

The distribution of cesium and ruthenium within the combustion train varied from run to run (Table 4). However, most of the ruthenium and cesium volatilized was condensed on the tube tip. Only at the high temperatures (1200 to 1400°C) was a significant amount of activity carried to the filter unit. Furthermore, most of the volatile activity was caught on the 40-μ-porosity nickel filter. In run 7, about 3% of the ruthenium and cesium did pass through the nickel filter to be collected on the paper filter. Operation of the nickel filter at 200°C instead of room temperature caused no apparent decrease in its efficiency. Gross beta and gross gamma analyses of the scrubber solutions were generally below the limits 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.

3.3 Dissolubility of the Combustion Ash

In each case the U_3O_8-Nb_2O_5 combustion ash was completely dissolved in 7 hr in refluxing 5 M HF--5 M HNO_3 (F/Nb mole ratio varied between 70 and 80). Complete dissolution in such a solution where the F/Nb mole ratio is greater than 60 was expected from prior work with unirradiated fuel samples.[3] The ash in each case was very friable and was easily poured from the reaction boat into the Teflon dissolver. These results indicate the chemical feasibility of a Burn-Dissolve process for Rover fuel if the combustion temperature is kept between 700 and 1400°C.

Table 3. Amounts of Fission Products Volatilized During Combustion of Kiwi-B4A Fuel Samples

Run	Temp. (°C)	Amount of Fission Product Volatilized (%)				
		Zr	Ce	Sr	Cs	Ru
1	700	0.003	0.008	0.09	0.21	35
3	700	0.003	0.04	0.02	1.1	65
9	700	0.13	0.08	0.09	0.59	57
2	900	0.009	0.007	0.03	0.33	82
4	900	0.005	0.008	0.08	2.0	89
5	1200	0.004	0.03	0.03	11.0	97
6	1200	0.005	0.01	0.03	1.6	93
7	1400	0.01	0.03	0.09	39	93
8	1400	0.02	0.02	0.04	0.98	100
10	1400	0.03	0.05	0.02	12	95

4. DISCUSSION

The results obtained in this study are in general agreement with those of a previous similar investigation[1] in which Kiwi-A fuel (burnup about 0.001%) specimens were burned in oxygen at about 900°C for 3 hr. The Kiwi-A specimens did not contain NbC, so the ash was essentially pure U_3O_8. 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.[12] The fuel pieces, which contained carbon-coated uranium dicarbide particles, were burned in air in the Oak Ridge Research Reactor for 15 min; the combustion temperature reached 1400°C. Little or no

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

Sample	Amount Found in Run (%)															
	1		2		3		4		5		6		7		8	
	Ru	Cs	Ru	Cs	Ru	Cs	Ru	Cs	Ru	Cs	Ru	Cs	Ru	Cs	Ru	Cs
Ash	65	99.8	18	99.6	35	99	10.7	98.1	3.4	89	7.2	98.4	6.5	60.6	0	99.1
Tube	--	--	7.8	--	4.5	0.5	11.7	1.4	8.5	2.2	5.5	0.4	60.5	35.6	28	0.9
Tube Tip	35	0.2	71	0.2	60.4	0.5	71	0.6	71.7	7.1	68.6	0.3	19.2	1.2	72	0.1
Metal Filter	--	--	3.2	t[a]	t	--	6.6	--	14	1.8	18.6	0.9	10.8	--	--	--
Paper Filter	--	--	--	--	--	--	--	--	2.4	--	0.05	--	3.0	2.7	--	--

[a] Trace.

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strontium, zirconium, barium, cerium, or uranium were volatilized; however, 35-40% of the cesium and 5-40% of the ruthenium were volatile.

The results of this study also agree qualitatively with those of a recent similar investigation[13] of the burning of HTGR fuel. The HTGR fuel, burnup about 10,000 Mwd/metric ton (Th + U), contained carbon-coated Th-U dicarbide particles (Th/U ratio of about 2.5) dispersed in a graphite matrix. Samples were burned for 5 hr at 800°C and 1200°C in the same equipment used in this study. Almost no uranium, thorium, zirconium, or rare earths volatilized. Greater than 78% of the ruthenium was volatile at 800°C, while at 1200°C its volatilization was 97 to 99% complete. Cesium was also appreciably volatile during combustion; 25-35% vaporized at 800°C, 67-88% at 1200°C. The reason for the much higher cesium volatility from the ThO_2-bearing ash is not immediately obvious. Perhaps sintering of Nb_2O_5 which melts at about 1450°C accounts partially for the retention of cesium by Rover ash; or, perhaps the analytical accuracy is enhanced with higher-burnup fuel. Further studies of the effect of ash composition on the retention of cesium would be highly desirable to resolve this point.

Although the present investigation was conducted with Rover fuel that did not contain coated particles, the general agreement with results of similar studies with coated-particle fuel should allow use of the data presented here for preliminary design of combustion facilities for the newer type of Rover fuel.

5. ACKNOWLEDGMENT

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6. REFERENCES

1. L. M. Ferris and L. A. Kambach, Uranium Recovery from Kiwi Fuel Elements: Laboratory Development, ORNL-3196 (Dec. 4, 1961).

2. L. M. Ferris, A. H. Kibbey, and K. S. Warren, Uranium Recovery from Kiwi-B Fuel Elements: Laboratory Development.Part II, ORNL-3283 (Nov. 16, 1962).

3. L. M. Ferris and K. S. Warren, Aqueous Processes for Uranium Recovery from Kiwi Fuel Elements: Laboratory Development. Part III, ORNL-3459 (in press).

4. Chemical Technology Division Annual Progress Report for Period Ending May 31, 1963, ORNL-3452 (suppl. 2) (in press).

5. L. E. McNeese and C. D. Scott, Recovery of Uranium from Graphite Fuels by Oxidation and Fluorination. I. Design and Initial Operation of Engineering-Scale Apparatus for Rover Fuel, ORNL-3434 (in press).

6. C. D. Scott, Recovery of Uranium from Graphite Fuels by Oxidation and Fluorination. II. Use of a Mathematical Analysis of the Oxidation Process in Fixed Beds to Predict Process Conditions, ORNL-3456 (in press).

7. T. A. Gens, Laboratory Development of Chloride Volatility Processes for the Recovery of Uranium Directly from Spent Rover Fuel or From Its Combustion Ash, ORNL-3376 (May 31, 1963).

8. T. A. Gens and T. B. Borne, Laboratory Development of a Process for Recovering Uranium from Rover Fuel by Combustion, Liquid-Phase Chlorination with Hexachloropropene, and Aqueous Extraction, ORNL-3435 (June 28, 1963).

9. Personal Communication, W. J. Martin, ORNL, to K. S. Warren, ORNL, September 16, 1963.

10. 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 (Feb. 14, 1961).

11. J. E. Sattizahn and G. F. Wagner, Radiochemical Measurements on Kiwi-B4A, LA-2897 (July 29, 1963).

12. ORNL Status and Progress Report, March 1963, ORNL-3436 (April 8, 1963).

13. L. M. Ferris, K. S. Warren, and J. W. Ullmann, Combustion-Dissolution Experiments with Irradiated Graphite-Base Reactor Fuel Containing Carbon-Coated Thorium-Uranium Dicarbide Particles, ORNL-TM-688 (in press).