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A BURN-LEACH PROCESS FOR RECOVERY OF URANIUM FROM ROVER FUEL: TERMINAL REPORT OF LABORATORY DEVELOPMENT

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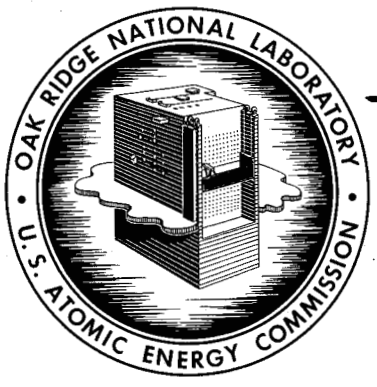

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ABSTRACT

Several aqueous methods for recovery of uranium from irradiated NbC-lined graphite-base Rover (nuclear rocket) fuels were evaluated on a laboratory scale. The burn-leach process, which is described in this report, is considered to be the simplest and best of the aqueous methods. In the first step of this process, the fuel is burned at 700 to 750°C, preferably in a fluidized-bed of inert alumina. Volatilization of all fission products except ruthenium is expected to be low during combustion. The fluidized-bed product is transferred to a leacher and is leached first with hot 6 to 10 M HNO_3 to recover 95 to 99% of the uranium; then, the residue is leached at 115°C with 10 M HNO_3--5 M HF (F/Nb mole ratio of about 10) to recover the remaining 1 to 5% of the uranium and practically all of the niobium. After leaching, the system is washed with water and all solutions are combined, along with the appropriate amount of aluminum nitrate solution, to produce a final solution having the composition 3 M HNO_3--1 M total F--0.06 M $UO_2(NO_3)_2$--0.1 M H_2NbOF_5--0.2 M $Al(NO_3)_3$. The uranium can be recovered from this solution and decontaminated by conventional tributyl phosphate solvent extraction procedures. Because the burnups of the Rover fuels are quite low (less than 0.04 at. %), plastic or plastic-lined vessels can be used for containing the highly corrosive HF-HNO_3 solutions in the leaching and feed adjustment steps. With aluminum nitrate present in the feed solution, rates of corrosion of types 309SCb and 347 stainless steels were less than 0.4 mil/month at room temperature, indicating that these alloys could be used as materials of construction for the solvent extraction system.

Combustion of Rover fuel in a fixed-bed burner at 700 to 800°C has also been studied. The U_3O_8-Nb_2O_5 combustion ash (even that produced at 1200 to 1300°C) can be dissolved in HF-HNO_3 (F/Nb mole ratio of about 10), using the two-stage leaching process. However, fixed-bed burning may not be as satisfactory as fluidized-bed burning because of engineering problems.

Direct leaching of the ash (from either a fluidized-bed or fixed-bed burner) with 10 M HNO_3--5 M HF is an alternative to the two-stage leaching procedure but is not as practicable. Uranium and niobium recoveries are slightly lower in the direct leaching method; furthermore, uranyl fluoride will precipitate from the leach solution unless it is diluted with water while still hot.

1. INTRODUCTION

The objective of the Rover project is to develop nuclear reactor engines for rocket propulsion.[1,2] From the inception of the program, graphite-base fuel elements have been used in the prototype reactors.[2]

Since 1957, Oak Ridge National Laboratory (ORNL) has been developing methods for recovering uranium from the prototype reactor fuels. Several different processes have been studied because the constitution of the fuel was changed periodically. The feasibility of two processes, burn-leach and combustion-fluoride volatility — which provide for practically quantitative recovery of the uranium from all types of graphite-base Rover fuels — has now been established. Both ORNL and Brookhaven National Laboratory (BNL) participated in the development of these processes. The burn-leach process involves combustion of the fuel at 700 to 750°C, preferably in a fluidized-bed of inert alumina, but possibly in a fixed-bed burner. The resultant bed or ash is then leached with an $HF-HNO_3$ solution to recover both the uranium and niobium. Evolution of the development of this process, and of the combustion-volatility process, has been described primarily in monthly status reports.[3-15] A bibliography of these and other reports covering the early phases of Rover fuel processing has also been issued.[16] The present report is a summary of all of the laboratory-scale work conducted at ORNL on the burn-leach process, and covers the period from April 1, 1963 to January 1, 1965.

The fuel elements for the current Rover reactors are 52-in.-long hexagonal rods (0.75 in. across the flats) consisting of carbon-coated uranium dicarbide fuel particles (beads) dispersed in a graphite matrix.[17] The beads are about 150 μ in diameter, with 25-μ pyrocarbon coatings. Each fuel rod has 19, 0.1-in.-diam cylindrical channels (holes) which are lined with NbC (1 to 3 mils thick) to prevent corrosion and erosion of the graphite by hydrogen, which is at once the reactor coolant and the rocket propellant. During fuel manufacture and reactor operation, 1 to 10% of the uranium is expected to migrate as carbide into the NbC liners. It is this uranium carbide, which apparently forms a solid

solution with the NbC, that complicates aqueous fuel processing. Leaching with nitric acid alone would be desirable after burning, but prior studies[18-22] have shown that the uranium is not completely recovered from the ash unless practically all the niobium oxide is dissolved. The uranium not recoverable by nitric acid leaching is assumed to be that which had migrated into the liner. The main objective in developing the burn-leach process, therefore, has been to determine conditions for dissolving both the uranium and niobium oxides after combustion of the fuel. Since niobium compounds are best dissolved in HNO_3-HF solutions, the effects of reagent composition, F/Nb mole ratio, reaction temperature, and reaction time on the leaching of typical combustion products were studied.

Fluoride volatility[3-15,21,24,25] and chloride volatility[5-15,21,26,27] methods have been considered for processing Rover fuels, along with several aqueous methods. The aqueous methods include grinding followed by acid leaching,[18,19,28,29] electrolytic disintegration,[18] disintegration-leaching with 90% HNO_3,[18,19,30] combustion in H_2SO_4-HNO_3 solutions,[5-8] combustion in molten nitrate systems,[8] and pressurized aqueous combustion.[11,13] None of these aqueous methods was completely satisfactory for coated-particle Rover fuels. Another process, the digest-burn-dissolve (DBD) process (formerly called the deline-burn-dissolve process) was developed[5-15,20,21] for processing the coated-particle Rover fuels. The chemistry in this process is similar to that in the burn-leach process; but, the DBD process is much more difficult to engineer than the burn-leach process.[14]

2. PROCESS FLOWSHEET

The two-stage leaching process suggested by BNL[3,4,22] affords the highest uranium and niobium recoveries, although satisfactory recoveries can be achieved in a single leach with HF-HNO_3 (Sec 4.3 and 4.4.2). A flowsheet for the two-stage leaching process using a fuel charge containing 1 kg of uranium is given as Fig. 1. The fuel (assumed to contain an average of 15% uranium and 10% niobium) is first chopped or crushed and then fed to a burner. Although the chemistry of the process is unaffected, fluidized-bed burning in an inert bed of alumina is assumed to be the best

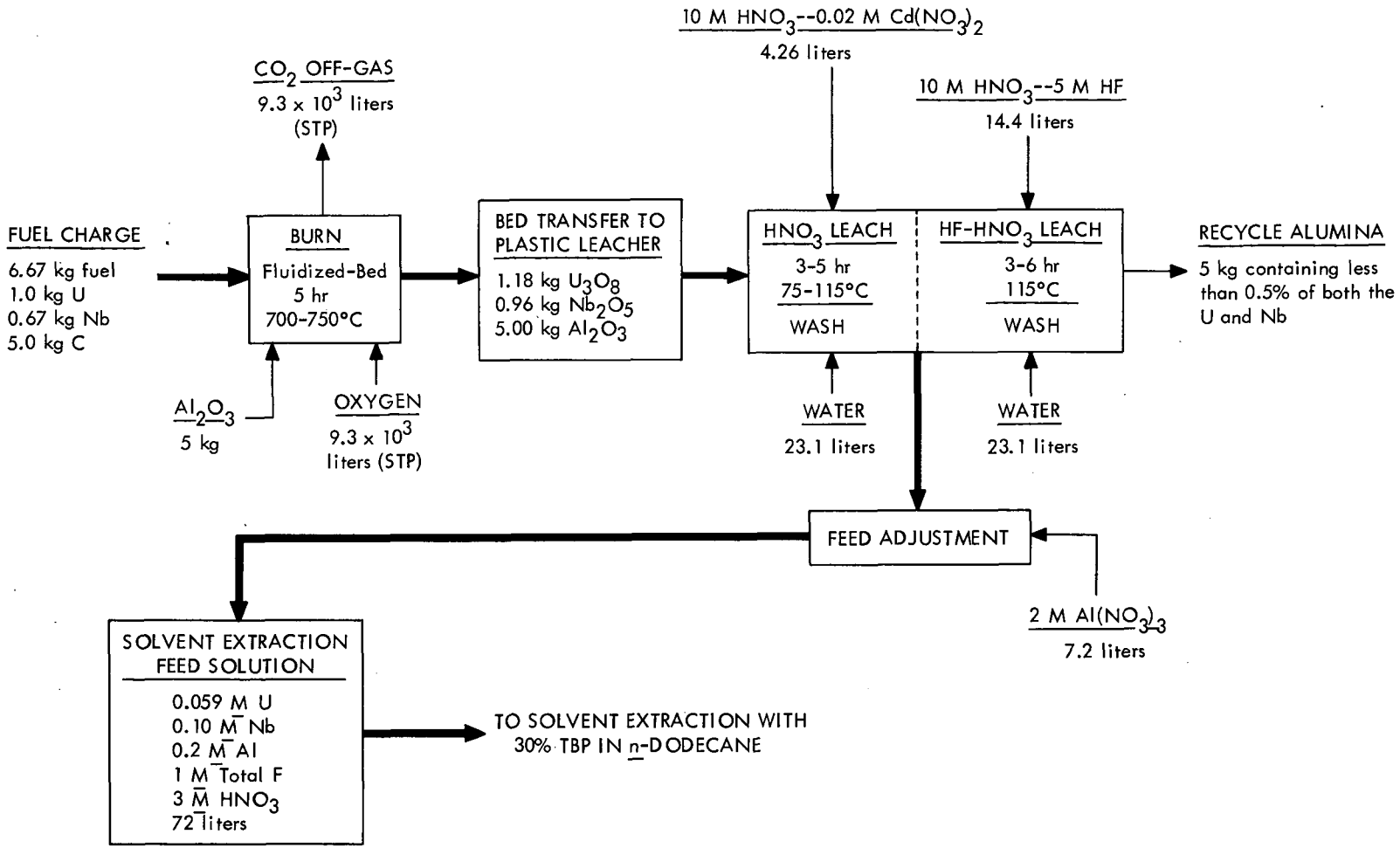

Fig. 1. Burn-Leach Process for Rover Fuels.

approach because of the ease of temperature control, ease of bed transfer, high reaction rates, and high oxygen utilization. The fluidized-bed burning could be conducted either continuously or semicontinuously; however, for convenience, the flowsheet is given for a batch or steady-state process. Burning is complete in about 5 hr, yielding a final bed containing about 30% U_3O_8 + Nb_2O_5. No studies have been made on the volatilization of fission products during fluidized-bed combustion. However, studies of the burning of small samples of irradiated Kiwi-B4A fuel in a tube furnace[23] showed that ruthenium is the only fission product that volatilizes to a significant extent at 700 to 800°C. Up to 65% of the ruthenium volatilized during combustion at 700°C, but the volatilized species were easily collected on a 40-μ-porosity nickel filter.

After burning, the bed is transferred to a plastic or plastic-lined leacher. Because the burnups of the Rover fuels are low (less than 0.04 at. %), Teflon can be used in the system without fear of radiation damage. The bed is then leached for 3 to 5 hr with 4.26 liters of 10 M HNO_3--0.02 M $Cd(NO_3)_2$ at 75 to 115°C. The cadmium serves as a soluble neutron poison. After washing with 23.1 liters of water, the bed is leached again for 3 to 6 hr with 14.4 liters of 10 M HNO_3--5 M HF at 115°C. This volume of HF-HNO_3 is sufficient to provide an F/Nb mole ratio* of 10. After a final water wash (23.1 liters), the solutions are combined to produce a solvent extraction feed solution having the composition 0.059 M U, 0.1 M Nb, 1 M total F, and about 3 M HNO_3. A small amount of aluminum nitrate can be added to this solution to complex most of the free fluoride, but care must be taken to avoid precipitation of the niobium as a slimy hydrous oxide (Sec 4.5). The aluminum nitrate also provides some salting strength for the solvent extraction feed. The leached alumina, which contains less than 0.5% of both the uranium and niobium, can either be recycled to the burner or discharged to waste. The fission product retention by the bed has not been measured but should be low. Less than 5% of the alumina is dissolved during leaching, giving an aluminum concentration of less than 0.07 M in the product solution. The uranium is decontaminated and recovered

*The F/Nb mole ratio is defined as the total number of moles of F in the system divided by the total number of moles of Nb in the system.

by solvent extraction with 30% TBP--70% n-dodecane followed by stripping with dilute nitric acid.[5,8,21]

3. EXPERIMENTAL

3.1 Fluidized-Bed Samples

Several different fluidized-bed samples were used in the leaching studies. Some of these were provided by BNL, the others by B. A. Hannaford, ORNL.[14,15] In each case, unirradiated Rover fuel specimens were burned in oxygen in a bed of Norton RR fused alundum (60 to 120 mesh) at 700 to 750°C. The compositions of the final bed materials are given in Table 1. The fuel specimens were not necessarily representative of those expected from reactor operation.

Table 1. Compositions of Fluidized-Bed Materials Used in Leaching Studies

Sample Code	Source	Composition of Bed (wt %)				Material Balance (%)
		U_3O_8	Nb_2O_5	Al_2O_3	C	
R-2	BNL	3.3	4.9	91	0.15	99.2
R-3-3	BNL	5.4	5.6	84	0.78	95.0
R-6	BNL	13.9	12.4	69	0.06	95.3
FB-2	ORNL	6.7	25.0	64	1.4	97.1
FB-3	ORNL	7.0	28.2	65	2.2	102.
FB-4	ORNL	15.3	17.6	64	1.9	98.5
FB-5	ORNL	20.5	9.2	62	--	92.1
FB-6[a]	ORNL	15.9	14.7	68	0.12	98.5
FB-C	ORNL	17.2	13.0	66	1.7	98.1
FB-HH[b]	ORNL	12.0	15.4	70	0.48	98.2

[a]Fuel used had been hot-H_2 tested at LASL for 80 sec at 2475°C.

[b]Fuel used had been hot-H_2 tested at LASL for 5 min at 2475°C.

For dissolution studies with ash similar to that expected from a fixed-bed burner, fuel samples were burned in a tube furnace in either pure oxygen or air. Generally, the composite ash from several samples was blended well to provide a single batch of oxide for use in the leaching experiments.

3.2 Apparatus and Leaching Procedure

Most of the leaching experiments were conducted in a Teflon system in which heated reagent was continuously circulated downward through a bed of sample by means of an air lift. This apparatus (Fig. 2) was similar to the type of leacher used at BNL and consisted of a 1/8-in.-thick, 12-in.-long reaction vessel which was surmounted by a Teflon condenser (A, Fig. 2). Both the condenser and reaction vessel were flanged and connected by friction sealing (B, Fig. 2). The reaction vessel was made from 3-in.-OD Teflon rod and had a 4.5-in.-long disengaging section (C, Fig. 2) above a 4.5-in.-long, 1-in.-OD leaching section (D, Fig. 2). The sample to be leached was supported by a Teflon sieve plate and Teflon wool filter (E, Fig. 2). Recirculation of the reagent was achieved through 0.25-in. Teflon tubing (F, Fig. 2) by injecting air, metered by a flowmeter (G, Fig. 2), into the lower end of the side-arm (H, Fig. 2). Most of the tubing was wrapped with Nichrome wire, which served as a resistance heater for the reagent.

Experiments were conducted by leaching 5- to 15-g samples of the bed materials or combustion ash with 30 to 50 ml of reagent. Reagent was pumped through the bed for the required time, and the resulting solution drained from the system by disconnecting the tubing at point I, Fig. 2. The leached bed was washed by pumping several portions of water through the bed and removing the wash water in the same manner as the leach solutions were removed. Generally, all the solutions were combined for analysis. After the bed was washed, it was poured out of the reaction vessel, dried at 110°C, weighed, and then analyzed.

Prior to use of the Teflon recirculating system, experiments were conducted in cylindrical Teflon pots[20] which were heated by heating mantles.

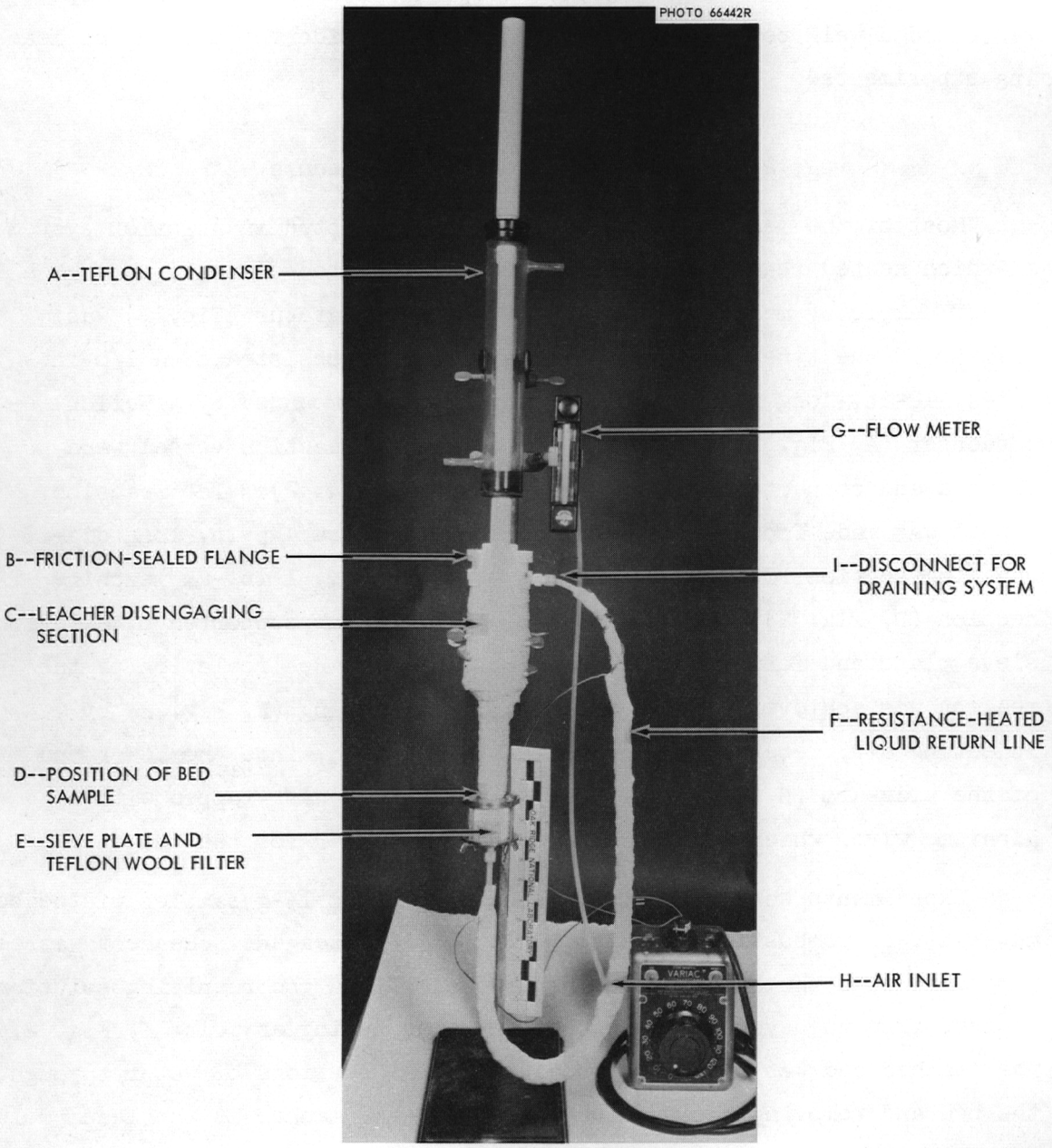

Fig. 2. Teflon Apparatus Used in Leaching Studies.

Magnetic stirrers were used in the pots at times in the hope of achieving good contact between the bed material and the leachant. Because of the small liquid volumes, compared with the sample sizes (about 1 ml for each gram of sample), required to achieve F/Nb mole ratios of about 10, this technique was highly unsatisfactory and led to erroneous results.[11-13] During leaching in the system agitated with a magnetic stirrer, some of the solution was splashed on the hot walls of the vessel above the liquid level and formed a crust (probably uranyl nitrate and niobic oxide). Apparently, only the uranyl nitrate was dissolved when the system was washed with water, since the niobium recoveries were much lower than those obtained in the recirculating reagent system, other conditions being the same.

4. RESULTS

4.1 Nitric Acid Leaching of Fluidized-Bed Products and Combustion Ash

The simplest and most desirable burn-leach process for Rover fuel would be combustion followed by leaching with nitric acid alone. Unfortunately, uranium losses to the residue generally were excessively high, even when the fuel was burned at low temperatures, 600 to 700°C. Although these experiments were conducted with unirradiated samples, the losses will probably be even higher with fuel that has been exposed to the operating temperature of the reactor where more extensive migration of the uranium into the NbC liner is expected. With typical fluidized-bed samples (Table 1) and nitric acid leaching, uranium recoveries varied from 90 to 99.7% (Table 2). These results are in good agreement with those obtained in pilot plant experiments at BNL.[22]

Uranium recoveries in the nitric acid leaching of ash, produced by combustion of Rover fuel samples in oxygen or air, in a tube furnace, were essentially the same as those obtained after fluidized-bed combustion. Burning at 600 to 700°C followed by leaching generally resulted in recoveries of 94 to 99.9% (Table 3). Similar experiments showed that the maximum uranium recoveries were obtained from ash produced at low temperatures. When the fuel was burned at high temperatures, or when

Table 2. Uranium Recoveries in Nitric Acid Leaching of Fluidized-Bed Products After Combustion of Rover Fuel

(Boiling reagent used in each experiment)

Expt.	Bed Sample	HNO_3 Conc. (M)	Time (hr)	Uranium Dissolved (%)
1	R-6	4	6	98.6
2	R-2	6	5	95.0
3	R-2	6	6	95.2
4	R-3-3	6	6	90.6
5	FB-2	10	6	94.4
6	FB-2	10	6	96.5
7	FB-2	10	6	96.8
8	FB-3	10	6	98.3
9	FB-4	10	6	98.9
10	FB-5	10	6	99.7
11	FB-6	10	6	98.9
12	FB-C	10	6	99.6
13	FB-HH	10	7	99.1
14	R-2	15.8	6	93.9

low-temperature ash was sintered at high temperatures, uranium recoveries were as low as 12% (Table 3). The low-melting Nb_2O_5 (m.p. about 1460°C[31]) apparently is easily sintered at temperatures above about 800°C and possibly tends to form a solid solution with U_3O_8 from which the uranium cannot be leached with nitric acid.

Several tests were made with hot-hydrogen tested fuel rods (rods which were heated to about 2475°C while a stream of hydrogen was being passed through the NbC-lined channels). The results of these experiments were inconclusive. For example, leaching of the ash produced by burning, at 700°C, of a rod that had been hot-hydrogen tested for only 80 sec at 2475°C, resulted in a uranium recovery of only 95%, whereas similar treatment of a rod hot-hydrogen tested for 5 min at 2475°C resulted in a uranium recovery of greater than 99%.

Table 3. Uranium Recoveries in Nitric Acid Leaching of Combustion Ash from Rover Fuel

(Samples burned in a tube furnace in O_2 or air; final solutions were 0.5 to 1 M in U)

Expt.	Combustion Temp. (°C)	Composition of Ash (%) U_3O_8	Composition of Ash (%) Nb_2O_5	HNO_3 Conc. (M)	Time (hr)	Uranium Dissolved (%)
1	600[a]	81	19	6	6	89.7
2	600[a]	57	43	6	6	95.0
3	625	57	43	4	6	99.6
4	625	57	43	5	6	99.8
5	700[a]	71	29	6	6	93.9
6	700[a]	74	26	6	6	83.2
7	700	56	44	6	5	94.0
8	800[a]	67	33	6	6	94.2
9	800	56	44	6	5	99.9
10	800	56	44	6	6	99.6
11	1000[a]	67	33	6	6	94.4
12	1000[a]	74	26	6	6	95.6
13	1000[b]	56	44	6	5	87.0
14	1200[b]	56	44	6	5	70.0
15	1260[c]	56	44	6	6	61.0
16	1400[b]	56	44	6	5	12.0

[a]Fuel samples in these experiments were from the thermally hot end of a hot-hydrogen rod tested for 80 sec at 2475°C.

[b]These samples were obtained by heating portions of the ash from experiment 7 for 3 hr in air at the indicated temperatures.

[c]This sample was obtained by heating a portion of the ash from experiment 9 to 1260°C in air.

4.2 Two-Stage Leaching of Fluidized-Bed Products

Studies at BNL[22] consisted of a two-stage leaching procedure where most of the uranium was leached from the bed with nitric acid and, then, the residual uranium and practically all of the niobium were dissolved in an HF-HNO_3 solution. BNL reported nearly quantitative uranium and

niobium recoveries. Similar experiments were conducted at ORNL which corroborated the BNL results. In the ORNL experiments, the bed was leached first with 10 M HNO_3 for 6 hr; then, the bed was leached for 6 hr at 115°C with 10 M HNO_3--5 M HF (F/Nb mole ratio of 10). Uranium and niobium recoveries were generally greater than 99.3% (Table 4). In experiment 3, the temperature of the HNO_3-HF leach was only 95°C, with a corresponding niobium recovery of only 63%. This experiment illustrates the need for conducting the HF-HNO_3 leach at or near the boiling point of the reagent (see also Sec 4.3.1). With boiling reagent (reaction temperature of about 115°C), 3 to 7% of the alumina was dissolved.

Table 4. Recoveries in Two-Stage Leaching of Fluidized-Bed Products

Expt.	Bed Sample	Amount Dissolved (%)		
		Uranium	Niobium	Aluminum
1	FB-2	99.7	99.3	7.0
2	FB-6	99.9	99.4	3.0
3	R-6	99.9	63.4[a]	1.2
4	R-6	99.9	98.6	---

[a]HF-HNO_3 leach conducted at 95°C in this experiment.

4.3 Direct Leaching of Fluidized-Bed Products

Direct leaching means that the bed material is leached only with HNO_3-HF solution prior to water washing. The results given below show that 99% of both the uranium and niobium can be recovered from typical bed materials in a single HF-HNO_3 leach, although the recoveries generally were lower than those obtained by the two-stage leaching procedure.

4.3.1 Effects of HF Concentration and Reaction Temperature on Direct Leaching of Uranium and Niobium with Solutions 10 M in HNO_3

Niobium and uranium recoveries were highest when the leachant (10 M HNO_3-HF) was at or near the boiling point and when the hydrofluoric acid

concentration in the leachant was greater than about 3 M. In each leaching experiment, the F/Nb mole ratio was 9 to 12, and the reaction time was 6 hr. The niobium recovery was highly dependent on the reaction temperature. For example, in 10 M HNO_3--5 M HF, the amount of niobium dissolved increased from 58 to about 99% as the leaching temperature increased from 75 to about 115°C (Table 5, Fig. 3). The amount of niobium dissolved at each temperature increased with increasing hydrofluoric acid concentration, although the most significant change occurred between 0 and 3 M (Fig. 3).

The uranium recoveries generally were greater than 99%, even when dissolution of the niobium oxide was incomplete, and were not greatly affected by variation in the leaching temperature between 75 and 115°C (Table 5). The high uranium recoveries were not unexpected because many of the fuel samples had little or no uranium associated with the NbC liners. Surprisingly, in some cases where more than 99% of the niobium oxide was dissolved, less than 98% of the uranium was recovered (Table 5). These experiments probably reflect analytical variations inherent in such complicated systems. The same argument is probably applicable to the high recoveries obtained with nitric acid alone from fuel hot-hydrogen tested for 5 min at 2475°C (experiment 13, Table 2).

In one experiment (experiment 20, Table 5), the leachant was made 0.03 M in $Cd(NO_3)_2$, which is an excellent soluble neutron poison. Although the recoveries were not as high as usually obtained, they were high enough to allow the conclusion that small amounts of cadmium in the leachant should not markedly affect the leaching procedure.

4.3.2 Effects of Nitric Acid Concentration and Reaction Time on Direct Leaching with Solutions 5 M in HF

The highest niobium recoveries were obtained in 5 M HF solutions when the nitric acid concentration was 10 M; however, the uranium recoveries, within experimental error, were not affected by increasing the nitric acid concentration from 4 to 10 M (Table 6). Samples of the FB-2 bed material were leached for 6 hr at 115°C in solutions where the hydrofluoric acid concentration was 5 M (F/Nb mole ratio of 9 to 12) and

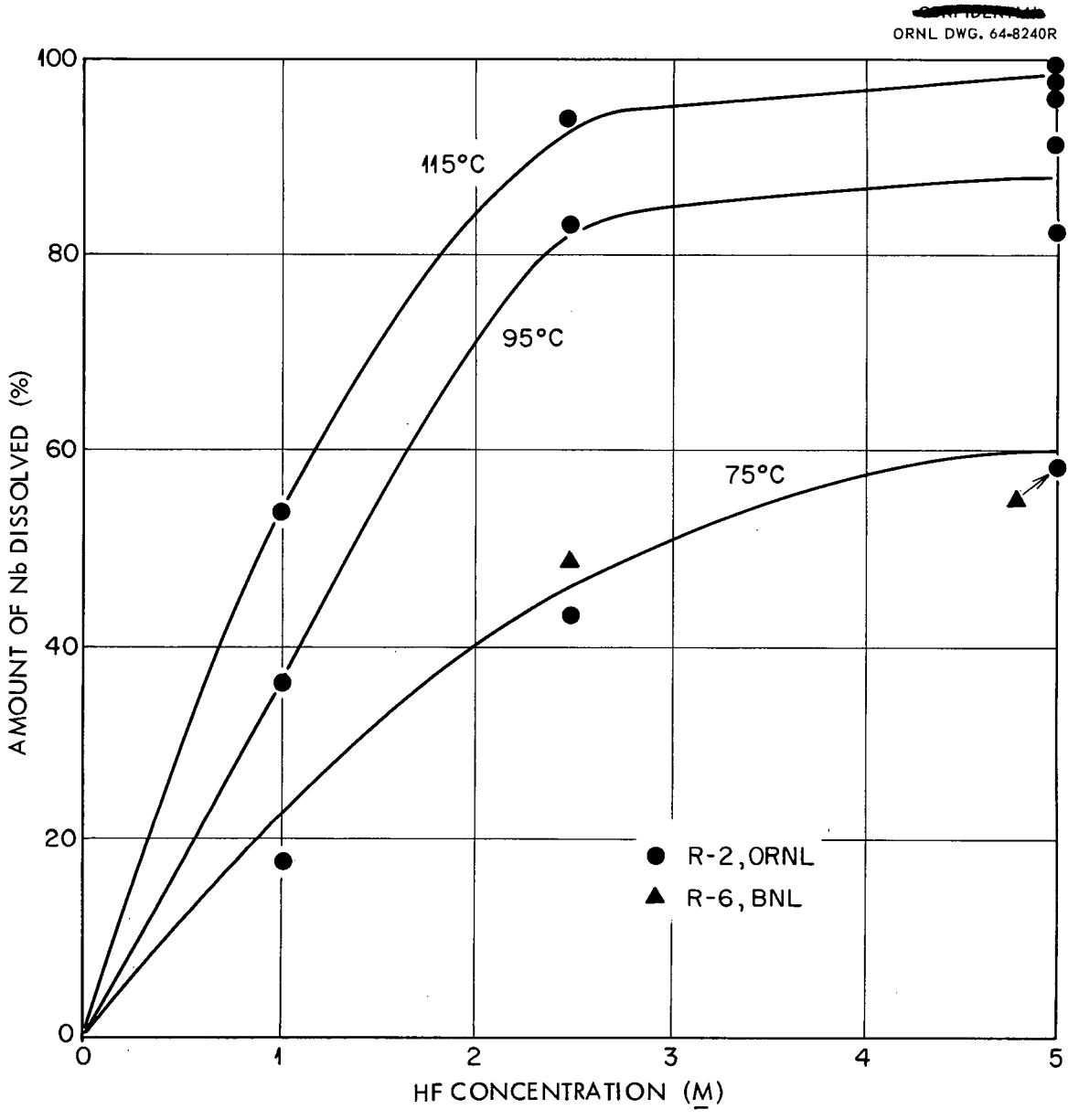

Fig. 3. Effects of HF Concentration and Temperature on Niobium Recoveries in HNO_3-HF Leaching of Fluidized Bed Samples after Burning of Rover Fuel. HNO_3 conc. = 10 M; F/Nb mole ratio = 9-12. Leaching time = 6 hr.

Table 5. Recoveries in the HF-HNO_3 Leaching of Fluidized-Bed Products (Leaching time = 6 hr; F/Nb mole ratio = 9 to 12)

Expt.	Bed Sample	Conc. in Leachant (M) HNO_3	Conc. in Leachant (M) HF	Temp. (°C)	Amount Dissolved (%) Uranium	Amount Dissolved (%) Niobium	Amount Dissolved (%) Aluminum
1	FB-2	10	1	75	96.7	18.3	3.2
2	R-6	10	2.5	75	99.0	48.5	1.3
3	R-6	10	2.5	75	99.9	19.6	0.9
4	FB-2	10	2.5	75	99.1	43.3	2.5
5	FB-2	10	5	75	99.1	58.4	1.4
6	FB-2	10	1	95	98.8	36.1	4.1
7	FB-2	10	2.5	95	99.4	83.4	2.4
8	FB-2	10	5	95	97.0	91.3	1.1
9	FB-2	10	5	95	97.9	82.5	0.85
10	FB-2	10	0	115	96.5	0.4	6.1
11	FB-2	10	0	115	94.4	0.0	0.48
12	FB-2	10	1	115	99.6	54.0	4.8
13	FB-2	10	2.5	115	99.6	94.2	2.0
14	FB-2	10	5	115	99.5	98.6	1.3
15	FB-2	10	5	115	99.7	97.6	1.2
16	FB-2	10	5	115	97.8	99.0	1.4
17	FB-3	10	5	115	95.7	99.3	1.3
18	FB-4	10	5	115	98.6	99.4	2.4
19	FB-6	10	5	115	99.3	99.1	1.8
20	FB-6	10[a]	5	115	98.0	90.3	2.4
21	FB-2	15	5	115	95.5	91.5	0.84
22	FB-2	10	10	115	92.6	99.5	0.30

[a]Reagent in this experiment was also 0.03 M in $Cd(NO_3)_2$.

the nitric acid concentration was varied from 2 to 10 M. The amount of uranium dissolved increased from 95 to about 99% as the nitric acid concentration increased from 2 to 4 M (Table 6). Similarly, the niobium recovery increased from 92 to about 99% as the nitric acid concentration

Table 6. Effect of HNO_3 Concentration on Leaching of Fluidized-Bed Sample FB-2 with 5 M HF--HNO_3 Solutions for 6 hr at 115°C (F/Nb mole ratio = 9 to 12)

Expt.	HNO_3 Conc. (M)	Amount Dissolved (%)		
		Uranium	Niobium	Aluminum
1	2	94.8	92.0	6.3
2	4	99.4	96.6	4.3
3	8	96.8	92.4	1.3
4	10	99.5	98.6	1.3
5	10	97.8	99.0	1.4
6	10	99.7	97.6	1.2

increased from 2 to 10 M. The niobium recovery was generally low when the nitric acid concentration in the leachant was greater than about 10 M (see, for example, experiment 21, Table 5). This behavior was probably caused by loss of HF from the system by volatilization, since the Teflon condensers were not particularly effective. In several experiments with leachants having nitric acid concentrations of 15 M, the F/Nb mole ratio dropped from an initial value of 10 to less than 5 in a 6-hr run. As expected, little niobium was solubilized in these experiments.

When 10 M HNO_3--5 M HF (F/Nb mole ratio of 9 to 12) was used as the leachant in experiments with the FB-2 bed material at 115°C, the amounts of both uranium and niobium dissolved increased from about 97 to 99% as the reaction time increased from 3 to 6 hr (Table 7).

4.3.3 Amount of Alumina Dissolved in HNO_3-HF Leaching of Fluidized-Bed Products

The amount of alumina that dissolved in a 6-hr leaching period decreased as the concentration of both the hydrofluoric and nitric acids in the reagent increased (Tables 5 and 6). Thus, with perhaps the optimum reagent 10 M HNO_3--5 M HF, only 1 to 2% of the alumina was dissolved. This corresponds to an aluminum concentration in the leach solution of about 0.1 M before dilution. It should be noted that these

Table 7. Effect of Time on Leaching Fluidized-Bed Sample FB-2 with 10 M HNO_3--5 M HF (F/Nb mole ratio = 9 to 12)
(Leaching temperature = 115°C)

Expt.	Leaching Time (hr)	Amount Dissolved (%)		
		Uranium	Niobium	Aluminum
1	3.0	96.6	96.6	1.3
2	4.5	94.6	98.2	1.4
3	6.0	99.5	98.6	1.3
4	6.0	99.7	97.6	1.2
5	6.0	97.8	99.0	1.4

results apply strictly to the Norton RR grade fused alundum used at both BNL and ORNL. A less-refractory grade of alumina might prove satisfactory for the combustion step, but, during leaching, could cause problems. If sufficient alumina were dissolved to produce a solution 0.3 M in aluminum or higher, the precipitation of hydrous niobic oxide could occur[20] (see also Sec 4.5).

4.4 Dissolution of Combustion Ash in HNO_3-HF Solutions

In the event that Rover fuel is burned in a fixed-bed burner rather than a fluidized bed, an ash consisting of only U_3O_8, Nb_2O_5, and fission product oxides would result. The results obtained in the HNO_3-HF leaching of the fluidized-bed products (Sec 4.3) showed that practically complete dissolution of both the uranium and niobium could be achieved in systems where the F/Nb mole ratio was about 10. Consequently, a few experiments were conducted to show that the same results could be obtained with combustion ash. The dissolubility of ash from unirradiated Rover fuel samples was studied previously, with somewhat conflicting results. In the previous work,[18-21] conducted in cylindrical Teflon pots, complete dissolution of the ash could not be achieved unless the F/Nb mole ratio was 60 or higher. As discussed in Sec 3.2, operation of the cylindrical pots was erratic when the volume-of-leachant to

weight-of-sample ratio was low (that is, when the F/Nb mole ratio was low), because of poor contact between the liquid and solids. When the F/Nb mole ratio was high (40 to 60), sufficient reagent was present to ensure that the sample was covered with liquid at all times. Thus, optimum recoveries were obtained only when the F/Nb mole ratio was high. The earlier studies also indicated that the hydrofluoric acid concentration of the reagent was not important at concentrations above about 1 M, a conclusion which is not valid based on the data given in Table 5 and Fig. 3.

4.4.1 Two-Stage Leaching of Combustion Ash

Following the same procedure used with the fluidized-bed samples (Sec 4.2), ash produced by burning Rover fuel was first leached for 6 hr in boiling 6 M HNO_3; then, the residue was dissolved in 10 M HNO_3--5 M HF (F/Nb mole ratio of about 10) in 6 hr. In both tests, complete dissolution of the ash was achieved:

Expt.	Ash Composition (%)		Amount Dissolved (%)	
	U_3O_8	Nb_2O_5	Uranium	Niobium
1[a]	47	53	100	100
2[b]	47	53	100	100

[a]Fuel sample burned in air at 625°C.

[b]The ash for this experiment was obtained by heating a portion of the ash from experiment 1 for 3 hr at 1260°C in air prior to leaching.

These results indicate that the two-stage leaching procedure will work as well on combustion ash as it does with fluidized-bed products. The results of experiment 2 suggest that complete dissolution can be accomplished even if the fuel is burned at 1200 to 1300°C.

4.4.2 Direct Dissolution of Combustion Ash

Several experiments were conducted to show that low-temperature (625 to 650°C) combustion ash could be dissolved directly in HF-HNO_3 solutions

when the F/Nb mole ratio was about 10. As experienced in the leaching of the fluidized-bed samples, uranium and niobium recoveries generally were slightly lower than those obtained with the two-stage leaching procedure. With boiling 10 M HNO_3--2.5 M HF or 10 M HNO_3--5 M HF, 96 to 100% of the uranium and 90 to 99.1% of the niobium were dissolved when the F/Nb mole ratio was 10 to 12 (Table 8). At 50°C, only 21.3% of the niobium was dissolved, as expected. These results are further confirmation of the fact that essentially complete dissolution of U_3O_8-Nb_2O_5 ash can be achieved in systems where the F/Nb mole ratio is about 10.

Table 8. Direct Dissolution of 47% U_3O_8--53% Nb_2O_5 Rover Combustion Ash in HNO_3-HF Solutions

Expt.	Conc. in Reagent (M) HNO_3	Conc. in Reagent (M) HF	Reaction Time (hr)	Temp. (°C)	F/Nb Mole Ratio	Amount Dissolved (%) Ash By Wt	Uranium	Niobium
1	10	2.5	6	50	12	62.6	99.9	21.3
2	10	2.5	6	115	11	98.6	99.8	99.1
3	10	5.0	6	115	10	97.0	99.9	94.0
4	10	5.0	6	115	10	100.	100.	100.
5	10	5.0	20	115	10	96.0	98.8	90.0

4.5 Stability Tests on Process Solutions

4.5.1 Stability of Leach Solutions

Leaching of typical fluidized-bed products with 10 M HNO_3--5 M HF or 10 M HNO_3--4 M HF (F/Nb mole ratios of about 10) yielded solutions having the approximate compositions 9 M HNO_3--5 M total F--0.5 M H_2NbOF_5--0.3 M $UO_2(NO_3)_2$ at the boiling point. Cooling such a solution to 50 to 60°C resulted in the precipitation of UO_2F_2. Although the UO_2F_2 is readily dissolved upon addition of wash water, the precipitation of solids, especially those containing uranium, must be provided for if a direct HF-HNO_3 leaching process is to be considered for Rover fuels.

4.5.2 Stability of Solvent Extraction Feed Solutions

The product solution from the burn-leach process would be diluted with water to 2 to 4 M HNO_3 and 1 to 1.5 M total F prior to decontamination and recovery of the uranium by solvent extraction with 30% TBP--70% n-dodecane solution. Such solutions are stable at room temperature. However, addition of aluminum nitrate to the solvent extraction feed solution is desirable because the aluminum nitrate not only provides higher extraction factors but also reduces corrosion of stainless steel equipment by complexing the free fluoride in the solution (only half of the total fluoride is complexed by the niobium when the F/Nb mole ratio in solution is 10). In earlier studies,[6,7,10] it was shown that some aluminum nitrate could be added to the feed solution, but the amount added had to be carefully controlled to avoid precipitation of niobic oxide. More detailed studies now show that sufficient aluminum nitrate can be added to a typical feed solution to produce a stable solution in which the free fluoride concentration is practically zero. The free fluoride concentration (Free F conc.) is defined as:

$$\text{Free F conc.} = \text{Total F conc.} - [5(\text{Nb conc.}) + 2(\text{Al conc.})] .$$

This definition of the free fluoride concentration is based on the assumption that the fluorine atoms in solution are present only as fluoride ions (F^-), $NbOF_5^{2-}$ ions, or AlF_2^+ ions.

For most of the tests, series of HNO_3-HF-H_2NbOF_5-$UO_2(NO_3)_2$-$Al(NO_3)_3$ solutions were prepared having total fluoride concentrations of 0.5, 1.0, or 1.5 M, and in which the F/Nb mole ratios were 10, and the U/Nb weight ratios were 1.51 (the approximate U/Nb weight ratio in Rover fuel). The effect of nitric acid and aluminum nitrate concentrations on the stability of the solutions at 25°C was then determined. If no precipitation occurred within five days, the solution was considered stable. One series of tests was made with solutions containing 3 M HNO_3, HF, and H_2NbOF_5, but no uranium.

With solutions having nitric acid concentrations of 2 to 4 M, the maximum aluminum nitrate concentration attainable without causing precipi-

tation of niobic oxide increased from about 0.15 to 0.45 M as the total fluoride concentration of the solution increased from 0.5 to 1.5 M (Table 9, Fig. 4). The aluminum nitrate concentration attained in solutions that were 1 M in HNO_3 was about 0.25 M when the total fluoride concentration was 0.5 M (Table 9, Fig. 4). The absence of uranium had no effect on the stability relationships in solutions that were 3 M in HNO_3 (Table 10, Fig. 5). Heating the stable solutions to 75°C did not cause precipitation.

In solutions in which the nitric acid concentration is 2 to 4 M, apparently about 2 moles of fluoride are complexed by each mole of aluminum, in addition to the 5 moles of fluoride complexed by each mole of niobium. This effect is illustrated in Fig. 6 which shows that HNO_3-HF-H_2NbOF_5-$UO_2(NO_3)_2$-$Al(NO_3)_3$ systems are unstable only when the calculated free fluoride concentration [Total F conc. - 5(Nb conc.) - 2(Al conc.)] is less than zero.

Neutron poisoning of the aluminum-bearing solvent extraction feed solutions is possible using cadmium nitrate, but not boric acid. Cadmium nitrate was easily dissolved at room temperature in 3 M HNO_3--1 M total F--0.07 M $UO_2(NO_3)_2$--0.125 M H_2NbOF_5--0.2 M $Al(NO_3)_3$ to give a Cd/U molar ratio of 1. Boric acid could not be added to the solution without causing precipitation.

4.6 Corrosion Studies Pertinent to Solvent Extraction

Because of the corrosivity of boiling HF-HNO_3 solutions, plastic or plastic-lined equipment will be required for the leacher and feed adjustment vessels in a burn-leach processing facility. However, it is highly probable that stainless steel, which is less expensive than plastic equipment, can be used for the solvent extraction equipment. Preliminary corrosion tests showed that type 309SCb stainless steel could probably be used for the extraction equipment at room temperature even if no aluminum nitrate were added to the feed solution. The expected rates of corrosion would be about 0.4 mil/month (Table 11). Addition of aluminum nitrate to a typical feed solution, 3 M HNO_3--1 M

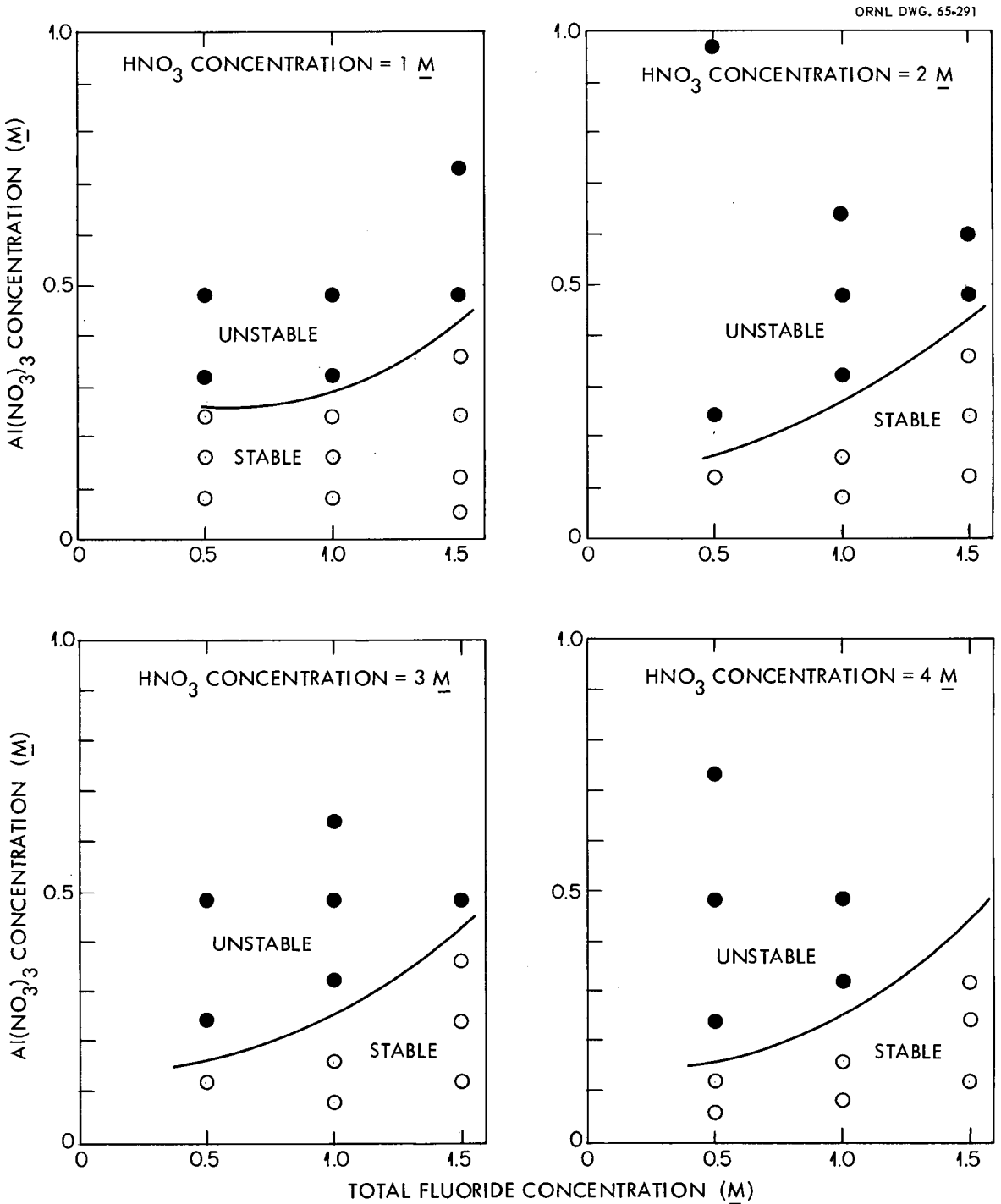

Fig. 4. Stability of HNO_3-HF-H_2NbOF_5-$UO_2(NO_3)_2$-$Al(NO_3)_3$ Solutions at 25°C. F/Nb mole ratio = 10 and U/Nb wt ratio = 1.5 in each solution; test period = 5 days.

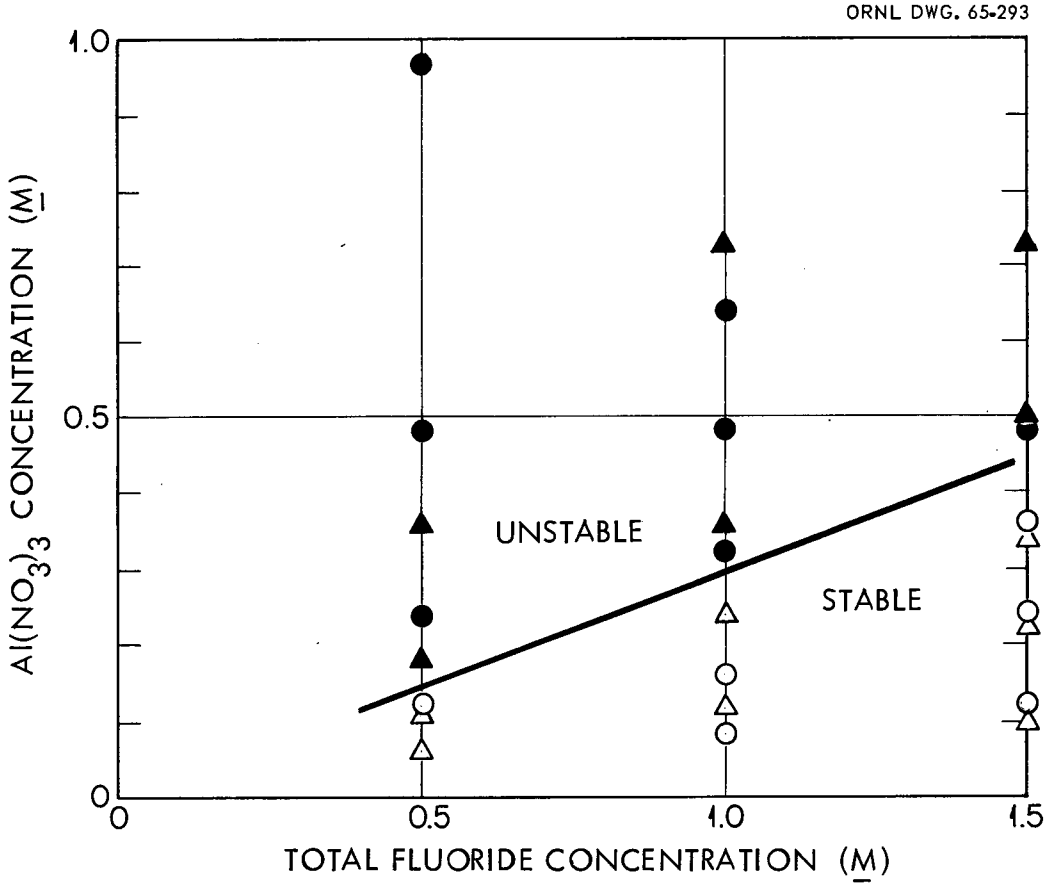

Fig. 5. Effect of Uranium Concentration on the Stability of HNO_3-HF-H_2NbOF_5-$UO_2(NO_3)_2$-$Al(NO_3)_3$ Solutions at 25°C. HNO_3 conc. = 3 M and F/Nb mole ratio = 10 in each solution; test period = 5 days. O,●: solutions in which U/Nb wt ratio = 1.5; △,▲: solutions containing no uranium.

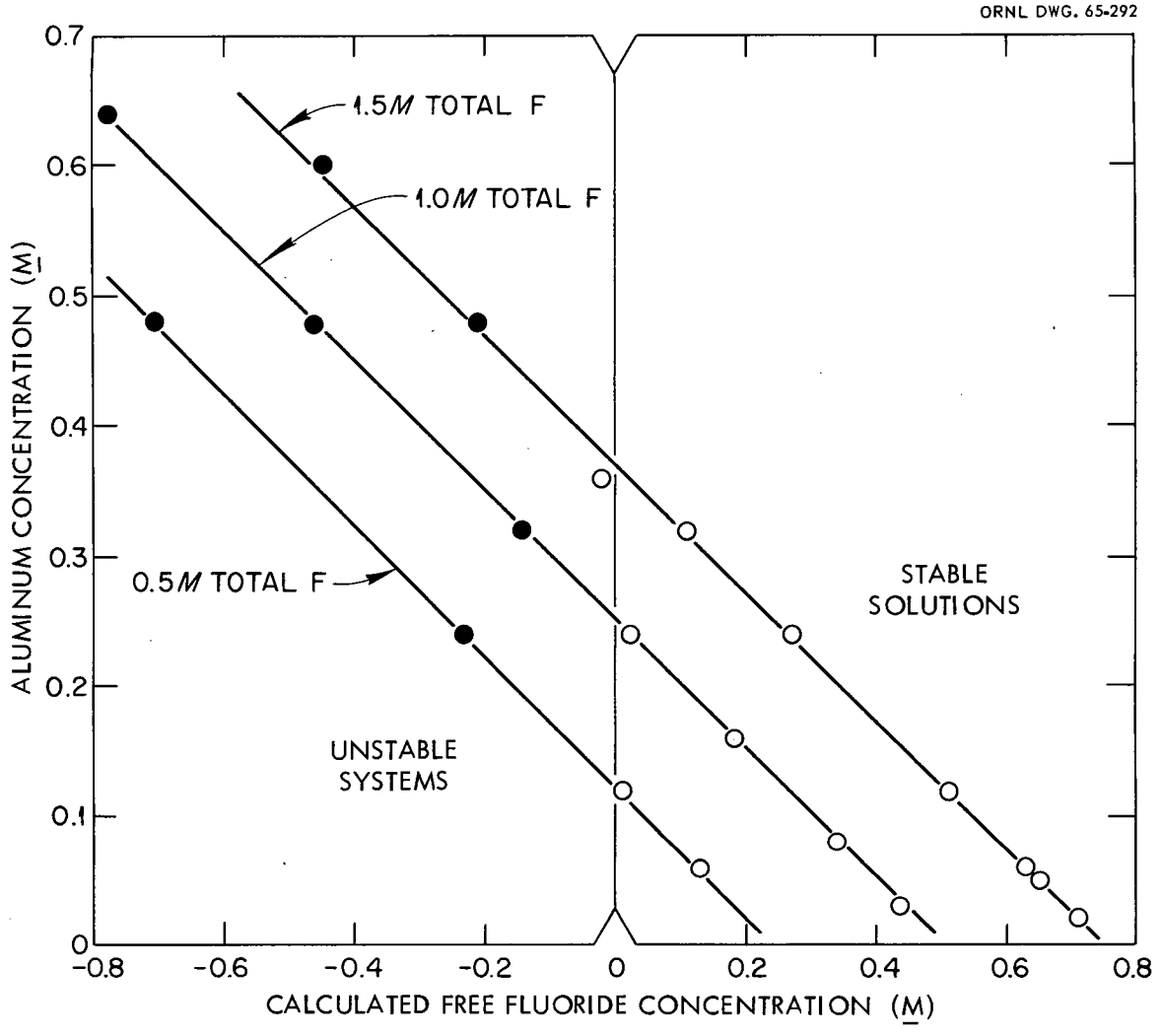

Fig. 6. Correlation Showing HNO_3-HF-H_2NbOF_5-$UO_2(NO_3)_2$-$Al(NO_3)_3$ Solutions to be Unstable when the Calculated Free Fluoride Concentration is Less Than Zero. Free fluoride concentration is defined as the total fluoride concentration minus [5(Nb conc.) + 2(Al conc.)].

Table 9. Stability of HNO_3-HF-H_2NbOF_5-$UO_2(NO_3)_2$-$Al(NO_3)_3$ Solutions at 25°C
F/Nb mole ratio = 10
U/Nb wt ratio = 1.51
Test period = 5 days

Concentration in Solution (M)			Free Fluoride Conc.[a] (M)	Stability of Solution[b]
HNO_3	Total F	$Al(NO_3)_3$		
1	0.5	0.48	-0.71	U
		0.32	-0.39	U
		0.24	-0.23	S
		0.16	-0.07	S
		0.08	0.09	S
		0.02	0.21	S
1	1.0	0.48	-0.46	U
		0.32	-0.14	U
		0.24	0.02	S
		0.16	0.18	S
		0.08	0.34	S
1	1.5	0.73	-0.71	U
		0.48	-0.21	U
		0.36	-0.02	S
		0.24	0.27	S
		0.12	0.51	S
		0.05	0.65	S
2	0.5	0.97	-1.69	U
		0.24	-0.23	U
		0.12	0.01	S
2	1.0	0.64	-0.78	U
		0.48	-0.46	U
		0.32	-0.14	U
		0.16	0.18	S
		0.08	0.34	S
2	1.5	0.60	-0.45	U
		0.48	-0.21	U
		0.36	-0.02	S
		0.24	0.27	S
		0.12	0.51	S
3	0.5	0.97	-1.69	U
		0.48	-0.71	U
		0.24	-0.23	U
		0.12	0.01	S
3	1.0	0.64	-0.78	U
		0.48	-0.46	U
		0.32	-0.14	U
		0.16	0.18	S
		0.08	0.34	S
3	1.5	0.48	-0.21	U
		0.36	-0.02	S
		0.24	0.27	S
		0.12	0.51	S
		0.06	0.63	S
4	0.5	0.80	-1.35	U
		0.73	-1.21	U
		0.48	-0.71	U
		0.24	-0.23	U
		0.12	0.01	S
		0.06	0.13	S
4	1.0	0.48	-0.46	U
		0.32	-0.14	U
		0.16	0.18	S
		0.08	0.34	S
		0.03	0.44	S
4	1.5	0.32	0.11	S
		0.24	0.27	S
		0.12	0.51	S
		0.06	0.63	S
		0.02	0.71	S

[a] Free fluoride concentration is defined as (Total F conc.) - [5(Nb conc.) + 2(Al conc.)] .

[b] U, unstable; S, stable.

Table 10. Effect of Uranium Concentration on the Stability of HNO_3-HF-H_2NbOF_5-$UO_2(NO_3)_2$-$Al(NO_3)_3$ Solutions at 25°C

HNO_3 conc. = 3 M
F/Nb mole ratio = 10
Test period = 5 days

Concentration in Solution (M)			Stability of Solution[a]
Total F	$UO_2(NO_3)_2$	$Al(NO_3)_3$	
0.5	0.0	0.36	U
	0.0	0.24	U
	0.0	0.18	U
	0.0	0.12	S
	0.0	0.06	S
	0.0	0.01	S
1.0	0.0	0.73	U
	0.0	0.48	U
	0.0	0.36	U
	0.0	0.24	S
	0.0	0.12	S
1.5	0.0	0.73	U
	0.0	0.48	U
	0.0	0.36	S
	0.0	0.24	S
	0.0	0.12	S
0.5	0.029	0.97	U
	0.029	0.48	U
	0.029	0.24	U
	0.029	0.12	S
1.0	0.059	0.64	U
	0.059	0.48	U
	0.059	0.32	U
	0.059	0.16	S
	0.059	0.08	S
1.5	0.088	0.48	U
	0.088	0.36	S
	0.088	0.24	S
	0.088	0.12	S
	0.088	0.06	S

[a] U, unstable; S, stable.

total F--0.07 M $UO_2(NO_3)_2$--0.125 M H_2NbOF_5, would be desirable if types 304L or 347 stainless steels were to be used. Without aluminum nitrate, the rates of corrosion of types 304L and 347 stainless steels were about 8 and 1 mils/month, respectively, in 1008-hr tests with welded specimens.

Table 11. Rates of Corrosion at 25°C of Welded 304L, 347, and 309SCb Stainless Steels in 3 M HNO_3--1 M total F--0.07 M $UO_2(NO_3)_2$--0.125 M H_2NbOF_5 With and Without Aluminum Nitrate

Test Period (hr)	Aluminum Conc. in Soln. (M)	Rate of Corrosion (mils/month)								
		309SCb			304L			347		
		V[a]	I[a]	S[a]	V	I	S	V	I	S
168	0	0.2	0.3	0.4	0.5	4.4	7.1	0.3	0.6	1.0
336	0	0.2	0.3	0.4	0.6	5.1	6.7	0.4	0.8	1.5
504	0	0.2	0.3	0.4	0.6	4.9	7.0	0.4	0.9	1.5
672	0	---	---	---	---	---	---	0.4	0.9	1.4
840	0	---	---	---	---	---	---	0.4	0.8	1.3
1008	0	0.2	0.3	0.4	0.6	5.0	8.0	0.4	0.8	1.2
168	0.2	---	---	---	0.4	1.4	2.1	0.2	0.3	0.3
336	0.2	---	---	---	0.3	1.1	2.0	0.2	0.3	0.3
504	0.2	---	---	---	0.3	1.0	2.0	0.2	0.3	0.3
672	0.2	---	---	---	0.3	0.8	1.7	0.2	0.2	0.2
840	0.2	---	---	---	0.2	0.7	1.6	0.2	0.2	0.2
1008	0.2	---	---	---	0.2	0.6	1.2	0.2	0.2	0.2

[a]Position of corrosion coupon: V, in vapor phase; I, at the liquid-vapor interface; and, S, in solution.

Making the solution 0.2 M in $Al(NO_3)_3$ reduced the rates of corrosion to about 1 and 0.2 mil/month, respectively (Table 11).

5. CONCLUSIONS AND DISCUSSION

The burn-leach process (two-stage leaching) appears to be the optimum aqueous process for graphite-base Rover fuels. All types of fuels, including those which did not contain coated fuel particles, can be processed by this method. Combustion in a fluidized-bed of inert alumina is the recommended burning procedure. Fluidized-bed burning provides for high oxygen utilization (BNL got 95% or better[22]), which minimizes the amount of off-gas that requires treatment, ease of temperature control

during burning, and, most importantly, ease of transfer of the bed to a plastic or plastic-lined leaching vessel. Furthermore, the fluidized-bed approach could probably be adapted for continuous operation. Combustion in a fixed-bed burner is less desirable, primarily because of the problem of ash transfer after combustion. No technique has yet been devised which would permit combustion of the fuel followed by dissolution of the ash in a single vessel.

The two-stage leaching procedure is recommended, even though adequate uranium and niobium recoveries can probably be achieved with a single HF-HNO_3 leach. The results of this study show that the recoveries are slightly higher for the two-stage procedure and that no problems with instability of uranium-bearing solutions exist. Most of the uranium is recovered in the first (nitric acid) leach. The nitric acid concentration and reaction temperature are not critical in this leach. High recoveries have been obtained with 6 to 10 M HNO_3 at temperatures from 50 to 115°C.[22] The optimum reagent for leaching the niobic oxide and the residual U_3O_8 from alumina beds in a system where the F/Nb mole ratio is around 10 is about 10 M HNO_3 which is 4 to 5 M in HF. With such a reagent, the maximum niobium recovery is achieved while attack of the alumina is minimized.

An alternative aqueous process, digest-burn-dissolve, also provides for practically quantitative recovery of uranium from all types of graphite-base Rover fuels.[20,21] The chemistry of the DBD process is essentially identical to that of the burn-leach process. However, the DBD process appears to be much more difficult to engineer.[14,32]

The most desirable aqueous process would involve combustion of the fuel followed by leaching with nitric acid alone. If adequate recoveries could be achieved by such a method, burning and leaching could be conducted in a single stainless steel vessel.[20] The Nb_2O_5 residue could be stored as a compact solid waste, and only relatively low-volume wastes would result from solvent extraction. This process has, at best, an outside chance of being feasible. Up to 10% of the uranium from the fuel beads is expected to migrate into the NbC liner during reactor operation and thus would be inaccessible to nitric acid even after the fuel is burned.

Furthermore, some evidence exists for the formation of nitric acid-insoluble U_3O_8-Nb_2O_5 solid solutions during combustion at 700 to 750°C. At BNL,[22] pilot plant studies were conducted with simulated fuel that had little or no uranium in the NbC liners prior to combustion. Yet, after burning, only 95 to 98.5% of the uranium could be recovered by nitric acid leaching, indicating that some interaction of U_3O_8 and Nb_2O_5 occurred during burning. Similar results were obtained in this study when fuel samples were burned at 600 to 800°C (see Sec 4.1). A more critical engineering evaluation of the aqueous processes for Rover fuels is being issued.[32]

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