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# URANIUM RECOVERY FROM KIWI-B FUEL ELEMENTS: LABORATORY DEVELOPMENT

## PART II


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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

# URANIUM RECOVERY FROM KIWI-B FUEL ELEMENTS: LABORATORY DEVELOPMENT. Part II


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## ABSTRACT

Laboratory-scale studies were made on aqueous dissolution methods for recovering uranium from NbC-lined KIWI B (graphite-base, uncoated particles) fuel elements.

Burning the fuel in oxygen and dissolving the ash completely in 1 to 21 M $HNO_3$ containing 1 to 5 M HF recovered the uranium quantitatively; complete dissolution required less than 5 hr when the F/Nb mole ratio was $\geq 60$

Mechanical grinding of fuel followed by a 6-hr leach with boiling 4 to 10 M $HNO_3$ containing 0.3 to 2 M HF resulted in uranium losses that decreased from 5 to 0.4% as the F/Nb mole ratio increased from 0 to 100 with -8 mesh fuel; the losses were half of those above when -50 mesh fuel was used. With two $HNO_3$-HF leaches and with a $HNO_3$ leach followed by a $HNO_3$-HF leach, losses were less than 0.1% with an overall F/Nb mole ratio of less than 6. Simultaneous disintegration and leaching with boiling 90 to 95% $HNO_3$ containing 0.5 to 2 M HF for 6 hr resulted in uranium losses that decreased from 3 to 0.4% as the F/Nb mole ratio increased from 0 to 35 and were only 0.05% with multiple leaching and a F/Nb mole ratio of less than 6.

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# URANIUM RECOVERY FROM KIWI-B FUEL ELEMENTS: LABORATORY DEVELOPMENT. PART II

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## 1.0 SUMMARY

Results of laboratory studies on aqueous methods for recovery of uranium from KIWI-B fuel elements are summarized. These fuel elements are lined with NbC but do not contain coated fuel particles. The methods studied, which precede decontamination and recovery of the uranium by solvent extraction, are: (1) combustion of the fuel followed by dissolution of the oxide ash in boiling $HNO_3$-HF solutions (this technique is also applicable to the advanced Rover elements which will contain carbon-coated $UC_2$ fuel particles); (2) grinding of the fuel followed by leaching with $HNO_3$-HF solutions (which is also applicable to coated particle fuels if they are ground fine enough to rupture the particles); and, (3) simultaneous disintegration and leaching in boiling 90-95% $HNO_3$ containing hydrofluoric acid (this technique is ineffectual with elements containing coated particles).

KIWI-B fuel burns rapidly in oxygen at temperatures above about 700°C. An excess of oxygen is required to minimize the amount of CO in the off-gas. The ash (about 50% $U_3O_8$, 50% $Nb_2O_5$) must be dissolved completely to ensure quantitative recovery of the uranium. Dissolution was complete in less than 5 hr in boiling 1 to 21 M $HNO_3$ containing 1 to 5 M HF when the F/Nb mole ratio was 60 or greater. At lower ratios, dissolution was incomplete in reaction times up to 24 hr. The rate of dissolution was not affected by variations in the nitric acid concentration and was virtually independent of the HF concentration in the range 1 to 5 M; however, dissolution was much slower when the HF concentration was less than 1 M. In processing, therefore, the dissolvent should contain at least 1 M HF ( with a F/Nb mole ratio of at least 60) and the nitric acid concentration should be chosen to optimize the solvent extraction conditions.

Because of the corrosiveness of $HNO_3$-HF solutions, the ash will probably have to be transferred from the metallic or ceramic burner to a

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plastic vessel for dissolution. Radiation damage to the plastic should not be a problem because of the low burnup of the Rover fuel elements. The dissolver could also be constructed of aluminum and, if the nitric acid concentration in the dissolvent were greater than 20 M, of stainless steel. Stability of the dissolver solutions is being studied in detail; the results will be reported later.

Combustion ash was also dissolved in 5 to 15 M $HF-H_2O_2$ solutions in about three hours. Complete dissolution and stable solutions were achieved when the F/Nb mole ratio was 8 to 10. This system should, therefore, receive more study to determine the minimum amount of fluoride ion required and to evolve a practicable solvent extraction method.

Recovery by $HNO_3$-HF leaching of uranium from mechanically-ground KIWI-B fuel elements (which do not contain coated fuel particles) depended on the following variables: F/Nb mole ratio, particle size of the fuel, leaching temperature, and mode of leaching. Variation of nitric acid and HF concentrations, in the ranges of 4 to 10 M and 0.3 to 2 M, respectively, had no effect on the leaching results; for the same particle size of feed, the F/Nb mole ratio was the most important variable. Single-batch experiments consisted of a 6- or 24-hr leach of the ground fuel followed by three water washes of the graphite residue. In 6-hr leaching experiments with fuel ground to pass an 8 mesh screen, the uranium lost to the residue decreased from about 5 to 0.4% as the F/Nb mole ratio increased from 0 to 100. Actually, increasing the ratio from 20 to 100 had little effect and increased the recovery by only 0.1%. Grinding to 50 mesh prior to leaching reduced the losses by about half, while leaching at 52°C instead of at the boiling point resulted in losses of about 2% even when the F/Nb mole ratio was 75. Leaching time was not an important variable; recoveries were unchanged when the digestion period was extended from 5 to 24 hr, other conditions being the same. In a few multiple-leach experiments using either successive $HNO_3$-HF leaches or a $HNO_3$ digestion followed by a $HNO_3$-HF leach, uranium losses were lower than those obtained in single-leach experiments where the F/Nb mole ratios were much higher. For example, leaching -16 mesh KIWI-B fuel twice for 4 hr with boiling 10 M $HNO_3$-0.5 M HF (total F/Nb mole ratio of 4) resulted in a uranium loss to the residue of only 0.01%. (A loss of

about 1.8% would be expected from a single 6-hr leach at this F/Nb mole ratio). Similarly, leaching of -8 mesh fuel for 4 hr with boiling 15.8 M $HNO_3$ (which recovered about 95% of the uranium) followed by a 4-hr leach with boiling 1 M $HNO_3$-3 M HF (F/Nb mole ratio of 3) resulted in a uranium loss of only 0.007%.

An optimized flowsheet for the Grind-Leach process is not yet possible since the factors influencing the stability of the leach solutions (particularly at low F/Nb mole ratios) are not fully understood. Preliminary work indicated that, in general, solutions in which the F/Nb mole ratio was less than about 20 were unstable, with precipitates forming. Since the niobium solubility in $HNO_3$-HF solutions at room temperature is about 1/5 the fluoride ion concentration, hydrolysis at higher temperatures probably accounts for the precipitation.

After leaching, separation of the powdered graphite residue from the product solution by vacuum filtration was difficult with fuel ground finer than about 10 mesh. However, centrifugation might be practicable for the solid-liquid separation. If centrifugation is feasible, additional pre-solvent extraction treatment of the process solutions could be considered. The addition of aluminum nitrate to the leach solutions resulted in precipitation of most of the niobium, without much ($<\sim 0.3\%$) attendent coprecipitation of the uranium. Aluminum nitrate addition would provide a solvent extraction feed which, in addition to being free of niobium, would not be very corrosive because of the complexing of fluoride ion by aluminum.

The Grind-Leach method is applicable, in principle, to the processing of the advanced Rover fuels, which will contain coated fuel particles. These fuels would have to be ground fine enough to ensure rupture of all the particles (probably to about 200 mesh). Grinding might be very difficult because of the extreme hardness of NbC, but the grinding could be simplified if the NbC liner were dissolved beforehand. If either filtration or centrifugation of the graphite-leach liquor slurry is unfeasible, the possibility exists of extracting the uranium directly from the slurry.

Another potential method for processing KIWI-B fuels which do not contain coated fuel particles involves simultaneous disintegration and

leaching in boiling 90 to 95% $HNO_3$ containing 0.5 to 2 M HF. With this procedure, mechanical grinding of the fuel is not necessary. Uranium recovery in the disintegration-leach process depended mainly on the F/Nb mole ratio, reaction temperature, and mode of leaching. With a 6-hr disintegration-leach, with boiling reagents, followed by three water washes of the residue, the uranium loss to the residue decreased from about 3 to 0.4% as the F/Nb mole ratio increased from 0 to 35; however, similar experiments at room temperature were ineffectual, the losses being 15 to 30%. As with the grind-leach method, preliminary experiments indicated that less fluoride ion would be required if successive leaches were used. The procedure involved a 4-hr disintegration step in 90% $HNO_3$, followed by addition of an equal volume of 1 M HF. Digestion was continued for an additional 3 hr, the solution was removed by vacuum filtration, and the cycle was repeated. In such an experiment with KIWI-B fuel, a uranium loss of only 0.05% was achieved when the total F/Nb mole ratio was only 6. By comparison, a loss of about 1.1% would be expected from a 6-hr disintegration-leach at the same F/Nb ratio.

Unlike the combustion-dissolution and the grind-leach techniques, the nitric acid disintegration-leach process does not appear to be adaptable to the processing of elements that contain coated fuel particles. The particle coatings are neither disintegrated nor oxidized by the nitric acid in a reasonable time.

## 2.0 INTRODUCTION

This report summarizes the results of laboratory-scale studies made during the period Sept. 1, 1961-July 1, 1962 on methods for recovering uranium from KIWI fuel elements, particularly KIWI-B. The KIWI reactors are prototypes of those to be used for nuclear space propulsion. Owing to the accelerated rate of reactor testing in the Rover nuclear rocket program, by 1966 several thousand kilograms of enriched uranium valued at $\$2$ to $3 \times 10^6$ will be associated with irradiated graphite-base KIWI test cores. Obviously, the economic incentive is great for immediate recovery of the uranium. The ORNL Chemical Technology Division was assigned the task of developing the chemical- and engineering-process flowsheet and preparing a preliminary design of the processing facility.

The fuel elements are fluted uranium-impregnated graphite tubes, 0.75 in. in diam and up to 52 in. long, containing 7 or 19 longitudinal passages to allow flow of the hydrogen propellant.[1-4] The passages are partially lined with 1- to 2-mil-thick NbC to prevent corrosion of the element in the high-temperature region of the reactor. The elements of the first series of reactors tested were made by blending uranium oxide and graphite powders, extruding the proper shape, and graphitizing at temperatures above 2100°C to form a nearly homogeneous dispersion of $UC_2$ in graphite. Niobium metal tubes were inserted in the propellant channels, and the elements were refired to about 1800°C to convert the liner to NbC. During the lining process, 2 to 5% of the uranium diffuses into the NbC, and a UC-NbC solid solution is formed. Recently, a major design change was made which affects elements for future Rover reactors. The elements will be the same shape and size as the earlier ones and will be lined with NbC, but the fuel will be pyrolytic carbon-coated $UC_2$ particles dispersed throughout the graphite matrix [5].

Various methods for processing such fuels, particularly Rover fuels, have been investigated at ORNL over the past several years[6-12]. Both aqueous and volatility methods are being evaluated, the aqueous to be followed by solvent extraction. Related work on Chloride and Fluoride Volatility processes will be reported separately.

The authors acknowledge the technical assistance of J. F. Land in conducting many of the experiments. Chemical and x ray analyses were made by the groups of W. R. Laing and R. L. Sherman of the ORNL Analytical Chemistry Division.

## 3.0 COMBUSTION-DISSOLUTION PROCESS

KIWI-B fuel burns rapidly in oxygen at temperatures above about 700°C. The resulting $U_3O_8$-$Nb_2O_5$ ash dissolves completely in less than 5 hr in boiling 1 to 21 M $HNO_3$ containing 1 to 5 M HF only when the F/Nb mole ratio is 60 or greater. This procedure should work equally well with NbC-lined Rover fuels that contain carbon-coated fuel particles.

### 3.1 Combustion

No systematic study of the variables affecting the rate of combustion was made. Kinetics of the graphite-oxygen reaction is the subject of several review articles.[10,13-15] The ignition temperature of KIWI-B fuel was determined, however, and was about 580°C (see Sect. 3.4).

### 3.2 Dissolution of KIWI-B in $HNO_3$-HF

Of several reagents tested only boiling $HNO_3$-HF and HF-$H_2O_2$ solutions completely dissolved KIWI-B combustion ash (about 50% $U_3O_8$, 50% $Nb_2O_5$). Leaching with boiling $HNO_3$, $HNO_3$-HCl, and $HNO_3$-$H_2SO_4$ solutions resulted in the dissolution of less than 1% of the $Nb_2O_5$, which retained up to 6% of the uranium (Table 1). Sintering of $Nb_2O_5$, which has the fairly low melting point of 1465°C [16] and subsequent entrapment of uranium (perhaps from the NbC-UC solid solution) during combustion is probably the reason why all the uranium cannot be leached from the ash with reagents which do not dissolve $Nb_2O_5$.

Table 1. Acid Leaching of $U_3O_8$-$Nb_2O_5$ Ash Produced by Burning KIWI-B Fuel Specimens in Oxygen

Leaching time, 5 hr

| Run No. | Comp. of Ash (%) U | Comp. of Ash (%) Nb | Boiling Reagent | Amount Retained by Acid-Insoluble Residue, (%) U | Amount Retained by Acid-Insoluble Residue, (%) Nb |
|---|---|---|---|---|---|
| 25 | 46.8 | 30.8 | 10 M $HNO_3$ | 3.75 | 99.9 |
| 11 | 42.4 | 33.0 | 3 M $HNO_3$-3 M HCl | 4.9 | 99.9 |
| 12 | 42.8 | 32.4 | 3 M $HNO_3$-3 M HCl | 4.6 | 99.8 |
| 13 | 41.9 | 32.7 | 10 M $HNO_3$-2 M $H_2SO_4$ | 4.8 | 99.7 |
| 14 | 42.2 | 32.9 | 5 M $HNO_3$-5 M $H_2SO_4$ | 5.7 | 99.5 |

Dissolution of the $Nb_2O_5$ portion of the combustion ash in $HNO_3$-HF solutions depended mainly on two variables, the F/Nb mole ratio and the HF concentration. The most important variable was the F/Nb mole ratio,

[redacted]

which is defined throughout this report as the ratio of total moles of fluoride ion in the dissolvent to the total number of moles of niobium in the fuel sample. The nitric acid concentration, which was varied from 1 to 21 M, had little, if any, effect on the dissolution. Furthermore, recovery of the last 5% of the uranium depended on the amount of niobic oxide dissolved. In order to recover 99.9% of the uranium from the ash, for example, at least 90% of the niobic oxide had to be dissolved (Fig. 1 and Table 2). In 5-hr experiments, complete dissolution was achieved only when the F/Nb mole ratio was 60 or greater; at these high ratios, variations in the hydrofluoric acid concentration produced no significant changes, the extent of dissolution being about the same in 1 and 5 M HF (Fig. 2). In nitric acid solutions containing 1 M HF the amount of $Nb_2O_5$ dissolved increased from about 2 to 100% as the F/Nb mole ratio increased from 2.5 to 60 (Fig. 2 and Table 2) which exemplifies the effect of the F/Nb mole ratio on the extent of dissolution. As an example of the effect of HF concentration, the amount dissolved in 5 hr increased from 0 to about 95% as the HF concentration increased from 0 to 5 M in solutions where the F/Nb mole ratio was 10 to 12 (Fig. 2).

Reaction time was not an important variable, about 2 hr being sufficient to allow the system to reach what apparently was a steady-state condition, other conditions being fixed. For example, in a series of experiments (runs 77-80, Table 2) with boiling 2 M $HNO_3$-2 M HF (F/Nb mole ratio of about 40) the amounts of $Nb_2O_5$ dissolved and the uranium recoveries were practically unchanged when the dissolution time was varied from 2 to 5 hr. Furthermore, other experiments under a variety of conditions showed that the amounts of uranium and niobium dissolved were not increased by increasing the reaction time from 5 to 24 hr (Table 2).

Precipitation of $NbO_2F \cdot 1/2\ H_2O$ and other unidentified species occurred in most $HNO_3$-HF solutions when the F/Nb mole ratio was less than 15. For more detailed discussion of the stability of the process solutions, see Sec. 4.5.

Since the nitric acid concentration had little effect on the dissolution, a suitable mode of operation might consist in the continuous

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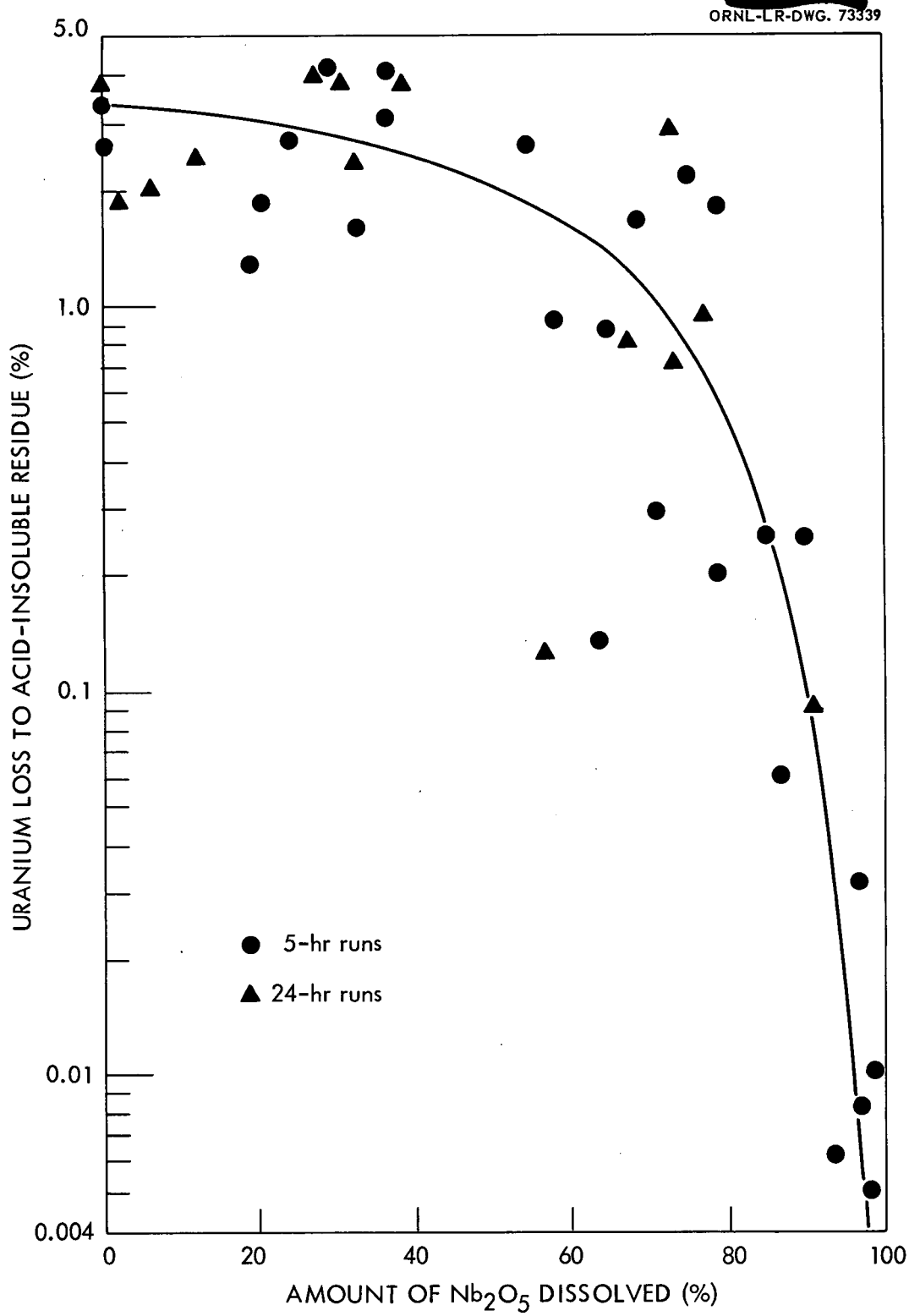


Fig. 1. Uranium losses to insoluble residues on dissolution of KIWI-B combustion ash (50% $U_3O_8$, 50% $Nb_2O_5$) in $HNO_3$-HF solutions.

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Table 2. Effect of HF Concentration, F/Nb Mole Ratio, and Reaction Time on the Dissolution of KIWI-B Combustion Ash in Boiling $HNO_3$-HF Solutions

| Run No. | Comp. of Ash, (%) U | Comp. of Ash, (%) Nb | Dissolvent, (M) $HNO_3$ | Dissolvent, (M) HF | F/Nb Mole Ratio | Reaction Time (hr) | Amt. Niobium Dissolved (%) | U Loss to Residue (%) |
|---|---|---|---|---|---|---|---|---|
| 25 | 46.8 | 30.8 | 10 | 0 | 0 | 24 | 0.08 | 3.75 |
| 1A | 45 | 30 | 10 | 0.5 | 2.5 | 5 | 0.03 | 3.18 |
| 6A | 43.5 | 33.0 | 10 | 1.0 | 2.5 | 5 | 2.3 | 3.60 |
| 2A | 45 | 30 | 10 | 0.5 | 5.0 | 5 | 3.8 | 2.58 |
| 26 | 43.5 | 33.4 | 15 | 0.5 | 5.0 | 5 | 0.20 | 3.35 |
| 27 | 43.6 | 32.7 | 21 | 0.5 | 5.0 | 5 | 0.39 | 2.61 |
| 5A | 47.2 | 34.8 | 10 | 1.0 | 5.0 | 5 | 36.8 | 2.20 |
| 23 | 45.6 | 32.6 | 3 | 1.0 | 5.0 | 24 | 32.5 | 2.34 |
| 32 | 47.5 | 30.3 | 4 | 0.5 | 5.6 | 5 | 24.8 | 4.28 |
| 34 | 46.1 | 29.7 | 4 | 0.5 | 5.7 | 24 | 27.1 | 3.99 |
| 43 | 46.2 | 29.7 | 10 | 0.5 | 5.7 | 5 | 24.2 | 2.74 |
| 45 | 46.0 | 28.8 | 10 | 0.5 | 5.9 | 24 | 12.7 | 2.48 |
| 52 | 48.5 | 30.2 | 4 | 3.0 | 5.6 | 5 | 65.2 | 0.86 |
| 54 | 46.1 | 29.7 | 4 | 3.0 | 5.7 | 24 | 67.8 | 0.80 |
| 62 | 48.6 | 29.0 | 10 | 3.0 | 5.8 | 5 | 19.1 | 1.28 |
| 64 | 45.5 | 29.6 | 10 | 3.0 | 5.7 | 24 | 7.7 | 1.28 |
| 56 | 46.1 | 30.2 | 4 | 5.0 | 5.6 | 5 | 64.0 | 1.33 |
| 58 | 44.8 | 26.8 | 4 | 5.0 | 6.3 | 24 | 77.4 | 0.94 |
| 37 | 47.8 | 25.5 | 4 | 1.0 | 6.9 | 5 | 36.7 | 4.07 |
| 39 | 46.3 | 24.1 | 4 | 1.0 | 7.0 | 24 | 30.8 | 3.76 |
| 48 | 45.9 | 21.3 | 10 | 1.0 | 8.0 | 5 | 21.0 | 1.85 |
| 50 | 40.4 | 25.7 | 10 | 1.0 | 6.6 | 24 | 2.3 | 1.42 |
| 24 | 44.3 | 34.2 | 10 | 1.0 | 10. | 24 | 73.7 | 0.72 |
| 31 | 48.2 | 30.0 | 4 | 0.5 | 11.3 | 5 | 37.3 | 3.16 |
| 33 | 46.2 | 29.7 | 4 | 0.5 | 11.4 | 24 | 38.8 | 3.72 |
| 42 | 47.6 | 28.7 | 10 | 0.5 | 11.8 | 5 | 33.1 | 1.60 |
| 44 | 44.6 | 28.4 | 10 | 0.5 | 11.9 | 24 | 2.6 | 1.91 |
| 36 | 46.7 | 29.5 | 4 | 1.0 | 11.4 | 5 | 69.1 | 1.68 |
| 38 | 47.9 | 29.0 | 4 | 1.0 | 11.6 | 24 | 73.3 | 2.82 |
| 47 | 46.1 | 23.9 | 10 | 1.0 | 14.2 | 5 | 71.2 | 0.29 |
| 49 | 48.6 | 27.6 | 10 | 1.0 | 12.3 | 24 | 9.4 | 0.68 |
| 51 | 48.3 | 31.2 | 4 | 3.0 | 10.8 | 5 | 86.8 | 0.06 |
| 53 | 47.4 | 29.2 | 4 | 3.0 | 11.6 | 24 | 90.6 | 0.09 |
| 61 | 47.0 | 30.9 | 10 | 3.0 | 10.9 | 5 | 2.0 | 0.80 |
| 55 | 47.0 | 31.0 | 4 | 5.0 | 10.9 | 5 | 93.7 | 0.06 |
| 3A | 45.5 | 29.0 | 10 | 0.5 | 15. | 5 | 60.3 | 0.77 |
| 21 | 44.9 | 21.0 | 4 | 0.5 | 16. | 24 | 6.5 | 2.07 |
| 22 | 43.2 | 22.2 | 10 | 0.5 | 15. | 24 | 6.2 | 1.59 |
| 4A | 53.1 | 37.1 | 10 | 1.0 | 15. | 5 | 72.0 | 0.26 |
| 41 | 47.5 | 33.8 | 10 | 0.5 | 20.1 | 5 | 58.2 | 0.90 |
| 30 | 48.3 | 30.6 | 4 | 0.5 | 22.2 | 5 | 54.6 | 2.61 |
| 3 | 52.0 | 34.6 | 10 | 1.0 | 24.5 | 5 | 90.0 | 0.25 |
| 35 | 46.4 | 26.7 | 4 | 1.0 | 25.3 | 5 | 79.3 | 1.79 |
| 46 | 47.9 | 25.8 | 10 | 1.0 | 26.2 | 5 | 75.3 | 2.26 |
| 19 | 42.3 | 34.3 | 3 | 3.0 | 20.0 | 5 | 98.5 | 0.0009 |
| 15 | 42.8 | 34.1 | 1 | 5.0 | 19.8 | 5 | 99.5 | 0.0013 |
| 7 | 39.1 | -- | 1 | 5.0 | 20 | 5 | -- | 0.13 |
| 20 | 45.7 | 33.8 | 3 | 3.0 | 30. | 5 | 99.2 | 0.0004 |
| 16 | 44.6 | 33.9 | 1 | 5.0 | 30. | 5 | 99.8 | 0.0013 |
| 10 | 43.0 | 19.5 | 3 | 3.0 | 35. | 5 | 97.0 | 0.032 |
| 4 | 54.9 | 19.7 | 3 | 1.0 | 43.0 | 5 | 79.0 | 0.20 |
| 1 | 52.4 | 27.4 | 10 | 1.0 | 40.5 | 5 | 98.9 | 0.01 |
| 77 | 48.2 | 34.4 | 2 | 2.0 | 39.4 | 2 | 89.7 | 0.32 |
| 78 | 47.4 | 32.7 | 2 | 2.0 | 41.4 | 3 | 97.1 | 0.46 |
| 79 | 46.4 | 33.8 | 2 | 2.0 | 40.1 | 4 | 93.2 | 0.21 |
| 80 | 48.6 | 35.0 | 2 | 2.0 | 38.7 | 5 | 92.3 | 0.37 |
| 9 | 45.4 | 25.5 | 3 | 3.0 | 40. | 5 | 98.2 | 0.005 |
| 2 | 58.8 | 23.5 | 3 | 1.0 | 47.2 | 5 | 85.2 | 0.25 |
| 76 | 44.8 | 25.9 | 10 | 5.0 | 52.2 | 5 | 3.8 | 0.87 |
| 75 | 47.1 | 25.7 | 10 | 3.0 | 52.6 | 5 | 30.8 | 0.29 |
| 85 | -- | 33.4 | 21 | 1.0 | 60.8 | 5 | >99. | 0.0 |
| 86 | -- | 32.9 | 21 | 1.0 | 61.5 | 5 | >99. | 0.0 |
| 88 | 59.0 | 32.8 | 4 | 1.0 | 62.1 | 5 | >99. | 0.0 |
| 90 | 56.5 | 31.2 | 4 | 5.0 | 65.2 | 5 | >99. | 0.0 |
| 89 | 53.5 | 31.0 | 4 | 3.0 | 65.6 | 5 | >99. | 0.0 |
| 81 | 49.6 | 30.5 | 2 | 2.0 | 66.5 | 5 | 100. | 0.00 |
| 87 | 53.0 | 27.9 | 4 | 0.5 | 72.6 | 5 | >99. | 0.0 |
| 82 | 48.6 | 35.3 | 2 | 2.0 | 76.7 | 5 | 100. | 0.00 |

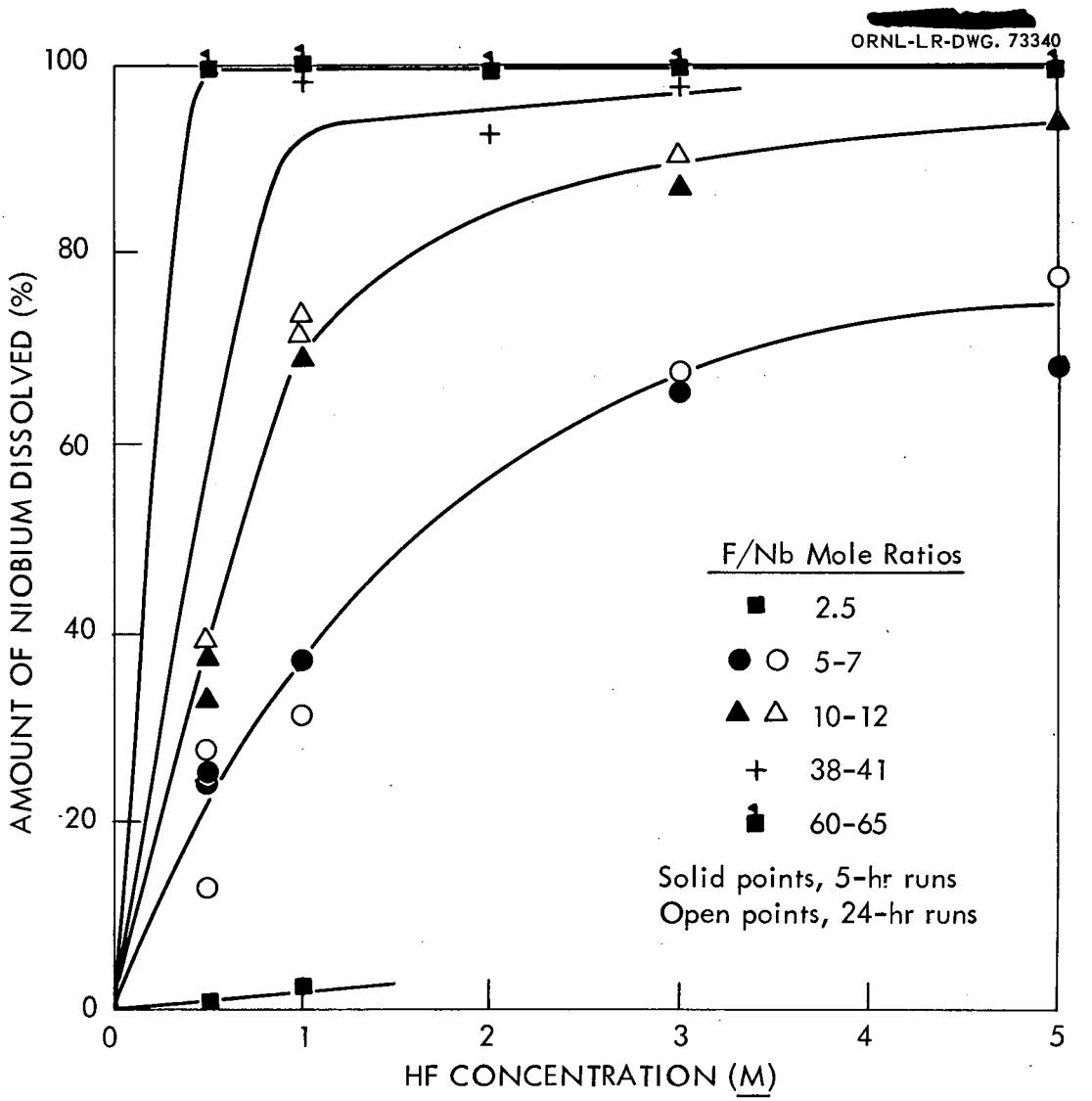


Fig. 2. Effect of F/Nb mole ratio and HF concentration on the dissolution of KIWI-B combustion ash (about 50% $U_3O_8$, 50% $Nb_2O_5$) in boiling $HNO_3$-HF solutions containing 4-10 M $HNO_3$.

addition of nitric acid to an HF dissolvent, mainly to effect dissolution of the $U_3O_8$ portion of the ash, or, the $HNO_3$ could be added at the end of an HF dissolution as in the ICPP process for zirconium fuels.[17]

Iron in amounts of 500 to 2000 ppm is a common impurity in Rover fuel elements. No troubles with insoluble, iron-bearing residues were experienced with the $HNO_3$-HF dissolution technique. Apparently, conditions suitable for the dissolution of niobic oxide are also suitable for the dissolution of the iron oxide.

### 3.3 Dissolution of Ash in HF-$H_2O_2$

Dissolution of the $U_3O_8$-$Nb_2O_5$ combustion ash was incomplete after a 5-hr digestion in boiling 5 M HF, as shown below.

| Run No. | F/Nb (mole ratio) | Amount of Nb Dissolved(%) | Uranium Loss to Residue (%) |
|---|---|---|---|
| 28 | 5.4 | 60.6 | 37.0 |
| 29 | 10.8 | 83.9 | 28.8 |

Although the F/Nb mole ratios in these two experiments were relatively low, the amounts of niobium and uranium dissolved increased when the ratio increased. Additional experiments will be required to determine whether the ash can be completely dissolved in HF alone if the F/Nb ratio is sufficiently high.

The ash can be dissolved in HF-$H_2O_2$ solutions. A sample of ash was digested in boiling 5 M HF (F/Nb mole ratio of 10) for 5 hr; then, a volume of 30% $H_2O_2$, equal to 1/7 the volume of the 5 M HF was added. Most of the green solid present at this point (probably mainly $UF_4$) was dissolved, but some white solids ($Nb_2O_5$?) remained. Both of these solids dissolved during a subsequent overnight digestion. The resulting solution was stable, at least for a few days, on cooling.

In similar studies at about 90°C,[18] it was found that the ash best dissolved in 13.5 M HF (F/Nb mole ratio of about 9) to which $H_2O_2$ was added intermittently to maintain constant volume. Dissolution was complete in less than 2 hr; the final solution contained 200 g of uranium per liter.

More effort should be devoted to the dissolution of the ash in HF-$H_2O_2$ since the amount of fluoride ion required for complete dissolution appears to be about six times lower than that required for $HNO_3$-HF dissolution. Plastic dissolvers should be as adaptable to the HF-$H_2O_2$ system as to the $HNO_3$-HF system, but methods for recovering the uranium from HF solutions by solvent extraction have not yet been fully investigated.

### 3.4 Low-Temperature Combustion

The combustion of graphite is straightforward in the laboratory but must be performed in an excess of oxygen to prevent the formation of CO, which can form explosive mixtures with oxygen. In general, the higher the burning temperature the more refractory the oxide ash would be expected to be because of the relatively low melting point of niobic oxide. The markedly different thermal and environmental conditions imposed in the two steps of the combustion-dissolution process probably preclude the use of a single vessel for the process. Low-temperature (less than 500°C) combustion might alleviate some of these conditions.

The addition of certain metal salts to carbon lowers the ignition temperature[19,20]. Preliminary experiments here showed that the ignition temperature of spectroscopic grade graphite and KIWI-B fuel specimens could be lowered by soaking the materials in solutions of lead, copper, manganese, or chromium salts. Lead acetate was the most effective in lowering the ignition temperature, as was found by Nebel and Cramer[20] for carbon black. Salts of iron and nickel were not effective in lowering the ignition temperature of the graphite, but iron salts were somewhat beneficial with KIWI samples.

KIWI-B fuel samples ignited at about 580°C in a stream of oxygen in the absence of catalytic metals. Soaking the fuel specimens in 0.07 M lead acetate, 0.25 M $KMnO_4$, or 3.15 M $Cu(NO_3)_2$ solutions lowered the ignition temperature 100 to 200°C (Table 3). The rate of combustion below the ignition temperature, however, was too low to be of practical value. For example, after soaking in copper nitrate solution, only about half the carbon (a 26% weight loss) was oxidized in 16 hr at 490°C, which is only 10°C below the ignition temperature.

Table 3. Low-Temperature Combustion of Graphite and KIWI-B Fuel Specimens after Soaking in Various Aqueous Solutions

| Material | Catalyst | Ignition Temp. (°C) | Combustion Temp. (°C) | Time (hr) | Weight Loss (%) |
|---|---|---|---|---|---|
| UCP Graphite[a] | None | 690 | 310 | 3 | 0.0 |
| | | | 330 | 3 | 0.0 |
| | | | 460 | 3 | 0.37 |
| | | | 460 | 3 | 0.05 |
| | | | 470 | 3 | 0.23 |
| | 0.07 M Lead acetate | 345 | 310 | 3 | 3.2 |
| | | | 330 | 3 | 6.0 |
| | 0.25 M $KMnO_4$ | 480 | 450 | 3 | 33.6 |
| | | | 460 | 3 | 34.4 |
| | 3.15 M $Cu(NO_3)_2$ | 480 | 460 | 3 | 13.5 |
| | | | 470 | 3 | 11.9 |
| KIWI-B Fuel | None | 580 | 460 | 16 | 3[b] |
| | | | 515 | 3 | 4.8 |
| | 0.07 M Lead acetate | 295 | 275 | 3 | -3 (wt. gain) |
| | | | 285 | 3 | -3 (wt. gain) |
| | 3.15 M $Cu(NO_3)_2$ | 500 | 450 | 3 | 1.5 |
| | | | 480 | 3 | 6 |
| | | | 490 | 3 | 7 |
| | | | 490 | 16 | 26 |
| | 0.25 M $KMnO_4$ | 520 | 460 | 3 | 5 |
| | | | 460 | 16 | 15 |
| | | | 490 | 3 | 5 |
| | | | 500 | 3 | 17 |
| | | | 510 | 3 | 15 |

[a] United Carbon Products Co. ultra purity spectroscopic graphite, Lot No. 5387, density, 1.55 g/c

[b] A 65 to 70% weight loss corresponds to complete combustion.

More spectacular results were obtained with spectrographic grade graphite. The United Carbon Products (UCP) graphite used ignited in oxygen at about 690°C (Table 3 and Fig. 3). Soaking the specimens in lead acetate, copper nitrate, or $KMnO_4$ solutions resulted in a lowering of the ignition temperature by 200 to 300°C. Furthermore, specimens treated with $KMnO_4$ burned fairly rapidly 30°C below the ignition temperature; in a 3-hr experiment at 450°C, a graphite specimen lost about 34% of its weight. These

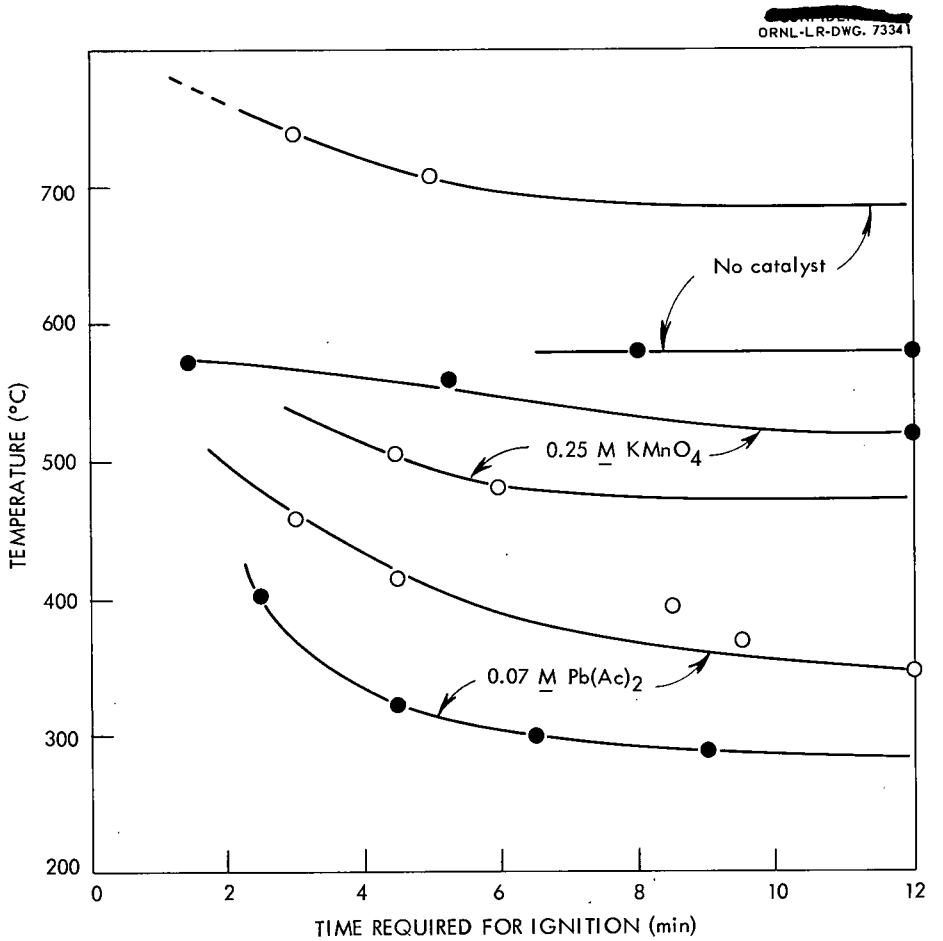


Fig. 3. Determination of ignition temperatures for KIWI-B fuel specimens and UCP spectrographic graphite after soaking in various solutions. Open points represent graphite specimens; solid points represent KIWI-B samples.

results, which were obtained first, prompted the studies with KIWI-B fuel.

Ignition temperatures were determined in the following manner: 1-inch lengths of spectroscopic graphite or 1/4-inch cross-sectional slices of KIWI-B fuel rods were immersed in the desired solution (the immersion time had no detectable effect on the ignition temperature) and then transferred to a tube furnace for measurement of the ignition temperature. The sample was then exposed to a stream of oxygen at various temperatures for periods up to 3 hr. The ignition temperature was approached from the region of higher temperature; that is to say, if the sample ignited (the surface glowed red and a blue corona developed around it) the temperature was low-

ered and a fresh sample tested As the ignition temperature was approached, the time required to ignite the specimen increased proportionately (Fig. 3); the ignition temperature was taken as the minimum temperature at which a sample actively burned when exposed less than 15 min. Numerous tests showed that conditions which inhibited ignition for 15 min generally suppressed ignition for a three hour period, the longest time that a test was conducted.

Temperatures were determined to $\pm 5^{\circ}C$ by inserting thermocouples directly in the graphite specimens as they were positioned in the furnace and calibrating another thermocouple which was adjacent to the wall of the tube. The calibration was necessary since it was impossible to insert thermocouples directly into the KIWI-B specimens.

The amount of salt sorbed during soaking was estimated by soaking the graphite samples in the various solutions for 16 hr, drying them at $110^{\circ}C$, and measuring the weight increase. The weight increases in $Cu(NO_3)_2$, lead acetate, and $KMnO_4$ solutions were 0.39, 0.17, and 0.47%, respectively. As mentioned above, the soaking time was not important; practically the same results were obtained by dipping the specimen into the solution for a couple of minutes and placing it directly in the furnace as with a 48-hr soak and preliminary drying prior to the combustion test.

Other procedures tried in an effort to lower the combustion temperature of KIWI-B fuel elements were: combustion in oxygen containing traces of $HNO_3$ vapor and burning in pure $NO_2$. The highest rate, about 2.8%/hr, was obtained with pure $NO_2$ at $500^{\circ}C$ and is considered too low to be of practical value (Table 4).

In preliminary experiments with another potential oxidant, $CO_2$, reaction rates with type GBF graphite were too low to warrant further study. The results are shown below.

| Temp. ($^{\circ}C$) | Reaction Time (hr) | Wt. Loss (%) |
|---|---|---|
| 800 | 3 | 0.6 |
| 900 | 3 | 0.7 |

Table 4. Reaction of KIWI-B Fuel with Oxygen Containing Nitric Acid Vapor and Pure $NO_2$

| Run No. | Oxidant | Temp. (°C) | Time (hr) | Wt. Loss (%) | Avg. Rate (%/hr) |
|---|---|---|---|---|---|
| 1X | Oxygen-$HNO_3$[a] | 400 | 6 | 2 | 0.33 |
| LT-4 | Oxygen | 500 | 4.7 | 0.54 | 0.11 |
| LT-3 | Oxygen-$HNO_3$[a] | 500 | 4.7 | 7.5 | 1.6 |
| 2X | $NO_2$ | 400 | 1 | 1.8 | 1.8 |
| 3X | $NO_2$ | 500 | 1.6 | 4.5 | 2.8 |

[a] Oxygen bubbled through 90% $HNO_3$ at room temperature.

## 4.0 GRIND-LEACH PROCESS

The Grind-Leach process[7-9,11] involves grinding of the fuel followed by leaching with boiling $HNO_3$-HF solution. This method is not applicable to fuels containing coated fuel particles unless they are ground fine enough to ensure rupture of all the particles, about 200 mesh. Uranium recoveries in 6-hr leaches of -8 mesh KIWI-B fuel (which did not contain coated fuel particles) with boiling 4-10 M $HNO_3$ containing 0.3-2 M HF increased from about 95 to 99.6% as the F/Nb mole ratio increased from 0 to 100. Slightly higher recoveries were obtained by leaching of fuel ground to 50 mesh. Uranium losses to the graphite residue were about 2% when -8 mesh fuel was leached for 6 hr at 52°C. Multiple-leach variations were also studied.

### 4.1 Conditions Affecting $HNO_3$-HF Leaching

#### 4.1.1 Effect of $HNO_3$ and HF Concentrations and F/Nb Mole Ratio

Using -8 mesh KIWI-B fuel samples, the effects of these three variables on the uranium recovery in a 6-hr leach with boiling reagent were studied. The nitric acid concentration, which was varied from 4 to 10 M, had no discernible effect on the uranium recovery, other conditions being the same (Table 5 and Fig. 4a). Similarly, variation in the HF concentration from 0.3 to 2 M had no effect on the uranium recovery at equal F/Nb mole ratios (Fig. 4b). The most important variable was the F/Nb mole ratio (the ratio of total fluoride ion in solution to total niobium in the fuel sample). The uranium loss to the graphite residue de-

Table 5. Effect of $HNO_3$ and HF Concentrations and F/Nb Mole Ratio on the Recovery of Uranium from -8 Mesh KIWI-B Fuel Samples with Boiling $HNO_3$-HF Solutions

Conditions: 6-hr leach; residue washed three times with cold water

| Run No., GL- | Fuel Comp. (%) | | Leachant (M) | | F/Nb Mole Ratio | Distribution (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Solution | | Residue | |
| | Uranium | Niobium | $HNO_3$ | HF | | U | Nb | U | Nb |
| 44 | 17.3 | 12.1 | 4 | 0 | 0 | 94.7 | 0.01 | 5.34 | 99.9 |
| 45 | 17.0 | 12.1 | 10 | 0 | 0 | 95.6 | 0.03 | 4.35 | 99.9 |
| 38 | 16.8 | 9.7 | 10 | 2.0 | 4.1 | 98.4 | 26.6 | 1.65 | 73.4 |
| 34 | 18.8 | 9.2 | 4 | 2.0 | 4.4 | 96.7 | 54.8 | 3.27 | 45.2 |
| 35 | 19.2 | 12.0 | 4 | 2.0 | 8.3 | 99.2 | 94.6 | 0.82 | 5.4 |
| 49 | 17.8 | 10.4 | 10 | 1.0 | 9.6 | 99.5 | 81.4 | 0.51 | 18.6 |
| 39 | 18.0 | 10.4 | 10 | 2.0 | 9.7 | 99.2 | 72.3 | 0.78 | 27.7 |
| 40 | 18.5 | 13.5 | 10 | 2.0 | 14.8 | 99.3 | 98.8 | 0.67 | 1.2 |
| 32 | 20.7 | 13.3 | 4 | 0.3 | 15.0 | 99.2 | 96.9 | 0.78 | 3.1 |
| 36 | 19.3 | 12.1 | 4 | 2.0 | 16.5 | 99.3 | 97.5 | 0.72 | 2.5 |
| 42 | 18.8 | 11.4 | 10 | 0.3 | 17.6 | 99.5 | 94.6 | 0.47 | 5.4 |
| 25 | 17.1 | 10.8 | 10 | 1.0 | 18.7 | 99.6 | 98.7 | 0.37 | 1.3 |
| 46 | 17.6 | 10.5 | 10 | 0.5 | 19.1 | 99.7 | 92.9 | 0.30 | 7.1 |
| 43 | 19.9 | 14.3 | 10 | 0.3 | 21.0 | 99.6 | 95.8 | 0.35 | 4.2 |
| 28 | 18.5 | 13.7 | 10 | 0.5 | 21.9 | 99.8 | 99.0 | 0.23 | 1.0 |
| 41 | 19.2 | 13.5 | 10 | 2.0 | 22.1 | 99.4 | 99.9 | 0.62 | 0.05 |
| 29 | 17.1 | 13.0 | 10 | 1.0 | 23.2 | 99.8 | 98.9 | 0.23 | 1.1 |
| 24 | 18.6 | 8.1 | 10 | 0.5 | 24.8 | 99.6 | 98.2 | 0.38 | 1.8 |
| 47 | 16.0 | 11.4 | 10 | 0.5 | 26.5 | 99.5 | 99.4 | 0.47 | 0.60 |
| 33 | 19.3 | 11.2 | 4 | 0.3 | 26.6 | 99.5 | 99.9 | 0.53 | 0.06 |
| 37 | 18.0 | 10.1 | 4 | 2.0 | 29.7 | 99.2 | 99.9 | 0.78 | 0.10 |
| 52 | 18.4 | 12.4 | 10 | 2.0 | 38.6 | 99.8 | 96.1 | 0.17 | 3.88 |
| 50R | 19.6 | 13.7 | 10 | 1.0 | 39.2 | 99.8 | 99.9 | 0.25 | 0.03 |
| 53 | 17.9 | 11.7 | 4 | 2.0 | 41.4 | 99.8 | 97.6 | 0.15 | 2.4 |
| 50 | 19.0 | 12.7 | 10 | 1.0 | 42.3 | 99.8 | 98.4 | 0.17 | 1.58 |
| 51 | 18.9 | 11.8 | 4 | 1.0 | 45.4 | 99.9 | 94.3 | 0.14 | 5.69 |
| 57 | 21.1 | 16.2 | 4 | 2.0 | 50.1 | 99.6 | 88.6 | 0.42 | 11.4 |
| 51R | 20.1 | 10.6 | 4 | 1.0 | 50.7 | 99.6 | 99.9 | 0.40 | 0.03 |
| 56 | 21.6 | 14.3 | 10 | 2.0 | 56.4 | 99.7 | 62.4 | 0.28 | 37.6 |
| 54R | 21.9 | 12.3 | 10 | 1.0 | 65.4 | 99.7 | 99.9 | 0.33 | 0.02 |
| 58RX | 17.8 | 15.7 | 10 | 1.0 | 68.6 | 99.5 | 99.5 | 0.53 | 0.55 |
| 59RX | 17.7 | 15.7 | 4 | 1.0 | 68.8 | 99.5 | 97.6 | 0.46 | 2.41 |
| 55R | 22.6 | 11.8 | 4 | 1.0 | 68.9 | 99.6 | 99.9 | 0.43 | 0.01 |
| 58R | 23.9 | 14.6 | 10 | 1.0 | 74.1 | 99.8 | 99.8 | 0.18 | 0.17 |
| 59 | 23.4 | 12.0 | 4 | 1.0 | 90.1 | 99.7 | 97.4 | 0.29 | 2.64 |
| 61 | 20.3 | 11.9 | 4 | 2.0 | 90.5 | 99.7 | 98.8 | 0.26 | 1.22 |
| 60 | 21.4 | 11.6 | 10 | 2.0 | 93.3 | 99.8 | 98.6 | 0.21 | 1.37 |
| 58 | 18.3 | 10.8 | 10 | 1.0 | 99.7 | 99.6 | 99.2 | 0.41 | 0.84 |

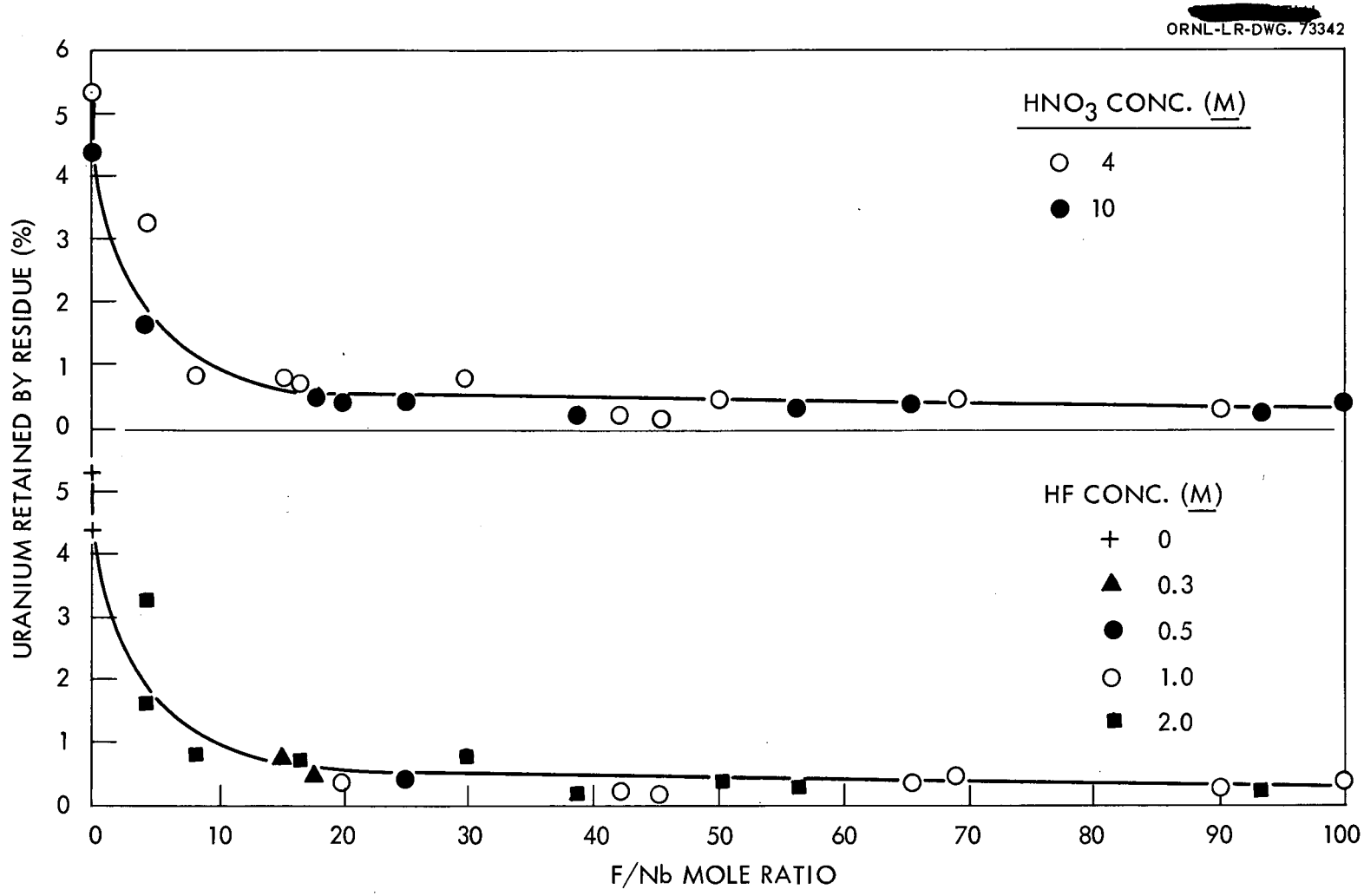


Fig. 4. Effect of F/Nb mole ratio, $HNO_3$ concentration (a), and HF concentration (b) on uranium losses to the graphite residue when KIWI-B fuel specimens (-8 mesh) were leached with boiling $HNO_3$-HF solutions for 6 hr. Each residue washed with 3 volumes of cold water prior to analysis.

creased from about 5 to 0.4% as the F/Nb mole ratio increased from 0 to 100 although, actually, increasing the ratio from 20 to 100 had little effect on the uranium recovery (Fig. 4 and Table 5).

### 4.1.2 Effect of Particle Size

In prior work on the leaching of graphite-base fuels, some increase in uranium recovery was obtained by finer grinding of the fuel[8,11]. This was also the case with KIWI-B samples. Leaching of intact 3- to 5-in. lengths of KIWI-B fuel with boiling $HNO_3$-HF for 6 hr recovered, at most, 83% of the uranium, as shown below.

| Run No., SC- | Fuel Comp. (%) | | Leachant (M) | | F/Nb Mole Ratio | Distribution, (%) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Solution | | Residue | |
| | U | Nb | $HNO_3$ | HF | | U | Nb | U | Nb |
| 1 | 16.7 | 14.0 | 10 | 2 | 35.5 | 82.8 | 99.8 | 17.2 | 0.25 |
| 2 | 17.7 | 13.7 | 4 | 2 | 38.7 | 55.8 | 99.8 | 44.2 | 0.23 |

Since most of the NbC liner was dissolved, the low recoveries in a single leach were probably due to the slow diffusion of reagent into or products out of the matrix. Similar work with intact fuel specimens showed that the uranium loss can be reduced to about 0.5% by using multiple leaches and washes[18,21]. Leaching intact fuel rods is analogous to leaching 4 to -6 mesh material since the shape of the rods is such that the maximum distance which the reagent or products must diffuse is about 4 mm.

As discussed in Sec. 4.1.1, losses as low as 0.4% were obtained with -8 mesh KIWI-B samples in a 6-hr leach if the F/Nb mole ratio was high enough. Grinding still finer, to 50 mesh, resulted in even lower uranium losses other conditions being the same. With the -50 mesh samples, the loss to the residue after leaching for 6 hr with boiling 4 M $HNO_3$-1 M HF and washing 3 times with water decreased from about 4 to 0.2% as the F/Nb mole ratio increased from 0 to 42 (Fig. 5 and Table 6). These losses are about half those obtained with the -8 mesh samples. Filtration of the slurries to prepare clear solutions for solvent extraction was very difficult, but centrifugation may be practical. Also direct extraction from the slurry was successful in laboratory-scale equipment[18,22].

[redacted]

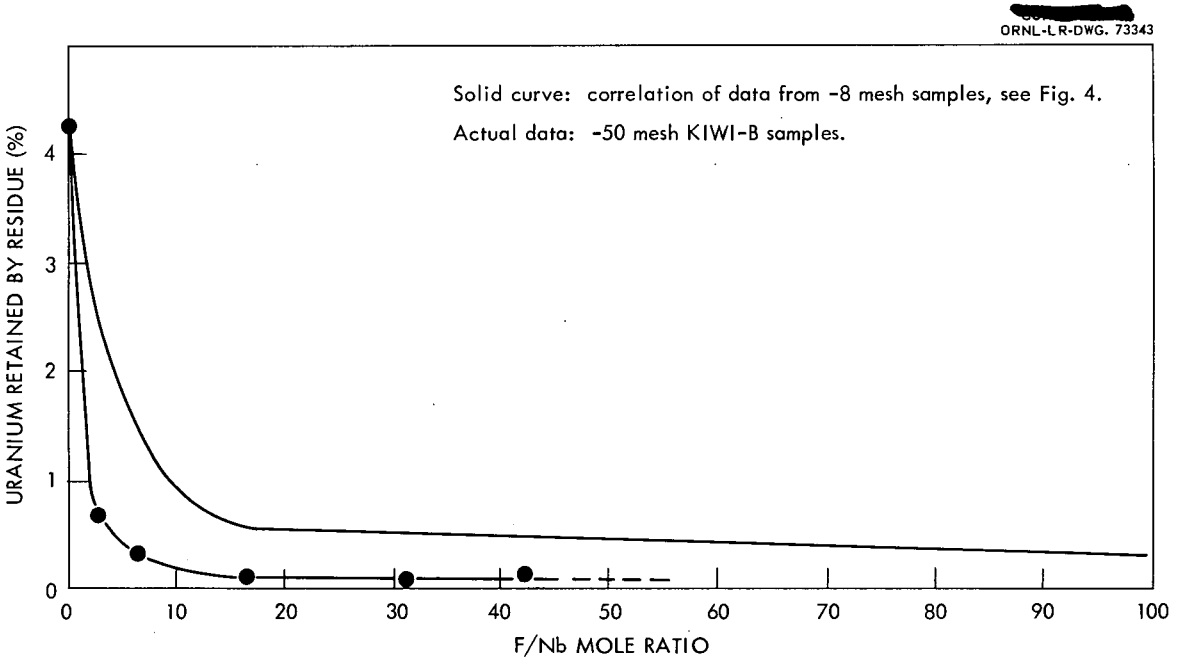


Fig. 5. Effect of particle size on uranium loss to residue in $HNO_3$-HF leaching of KIWI-B fuel samples. The -50 mesh samples were leached with boiling 4 M $HNO_3$- 1 M HF. Leaching time in all cases, 6 hr.

Table 6. Effect of F/Nb Mole Ratio on the Recovery of Uranium from -50 Mesh KIWI-B Fuel Samples with Boiling 4 M $HNO_3$- 1 M HF Solutions

Conditions: 6-hr leach; residue washed 3 times with cold water

| Run No. | Fuel Comp. (%) | | F/Nb Mole Ratio | Distribution, (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Solution | | Residue | |
| | U | Nb | | U | Nb | U | Nb |
| GL-68[a] | 18.7 | 9.1 | 0 | 95.7 | 0.34 | 4.27 | 99.7 |
| GL-62 | 16.0 | 9.5 | 2.8 | 99.3 | 14.0 | 0.68 | 86.0 |
| GL-63 | 16.0 | 10.4 | 6.5 | 99.7 | 82.1 | 0.32 | 17.9 |
| GL-64 | 19.5 | 8.1 | 16.6 | 99.8 | 98.9 | 0.23 | 1.1 |
| GL-65 | 20.7 | 8.6 | 31.4 | 99.8 | 99.4 | 0.20 | 0.64 |
| GL-66 | 20.4 | 9.6 | 42.4 | 99.8 | 98.0 | 0.25 | 2.0 |

[a] Leachant in this run was boiling 4 M $HNO_3$.

### 4.1.3 Effect of Digestion Time

Only a few experiments were conducted with -8 mesh KIWI-B samples to determine the effect of digestion time; in these, there was no beneficial effect in increasing the digestion time from 6 to 24 hr in solutions having the same F/Nb mole ratio (Table 7).

Table 7. Effect of Leaching Time on the Recovery of Uranium from -8 Mesh KIWI-B Fuel Samples with Boiling $HNO_3$-HF Solutions
Conditions: residue washed 3 times with water after each leach

| Run No. | Fuel Comp. (%) | | Leachant (M) | | Time (hr) | F/Nb Mole Ratio | Amount in Residue (%) | |
|---|---|---|---|---|---|---|---|---|
| | U | Nb | $HNO_3$ | HF | | | U | Nb |
| GL-36 | 19.3 | 12.1 | 4 | 2.0 | 6 | 16.5 | 0.72 | 2.5 |
| GL-26 | 18.4 | 12.4 | 10 | 0.5 | 24 | 16.1 | 0.33 | 1.2 |
| GL-25 | 17.1 | 10.8 | 10 | 1.0 | 6 | 18.7 | 0.37 | 1.3 |
| GL-27 | 17.7 | 10.9 | 10 | 1.0 | 24 | 18.3 | 0.49 | 15.9 |
| GL-30 | 18.8 | 13.1 | 10 | 0.5 | 24 | 22.9 | 0.24 | 1.1 |
| GL-29 | 17.1 | 13.0 | 10 | 1.0 | 6 | 23.2 | 0.23 | 1.1 |
| GL-31 | 18.6 | 12.8 | 10 | 1.0 | 24 | 23.4 | 0.61 | 5.6 |

### 4 1.4 Effect of Digestion Temperature

Most metallic materials of construction are severely corroded by boiling $HNO_3$-HF solutions, but, possibly, aluminum or stainless steel could be used for the Grind-Leach process at temperatures below about 60°C[18,22,23]. A series of $HNO_3$-HF leaching experiments with -8 mesh KIWI-B fuel samples was conducted at 52°C to see if high uranium recoveries could be achieved at this lower leaching temperature. In 6-hr leaches followed by three water washes, uranium losses to the graphite residues decreased from about 8 to 2% as the F/Nb mole ratio increased from 0 to 75 (Fig. 6 and Table 8). These losses were 2 to 4 times greater than obtained under the same conditions with boiling reagents (Fig. 6). However, in the 52°C experiments, the NbC liner usually was dissolved so that multiple leaching at lower temperatures might yield suitable uranium recoveries.

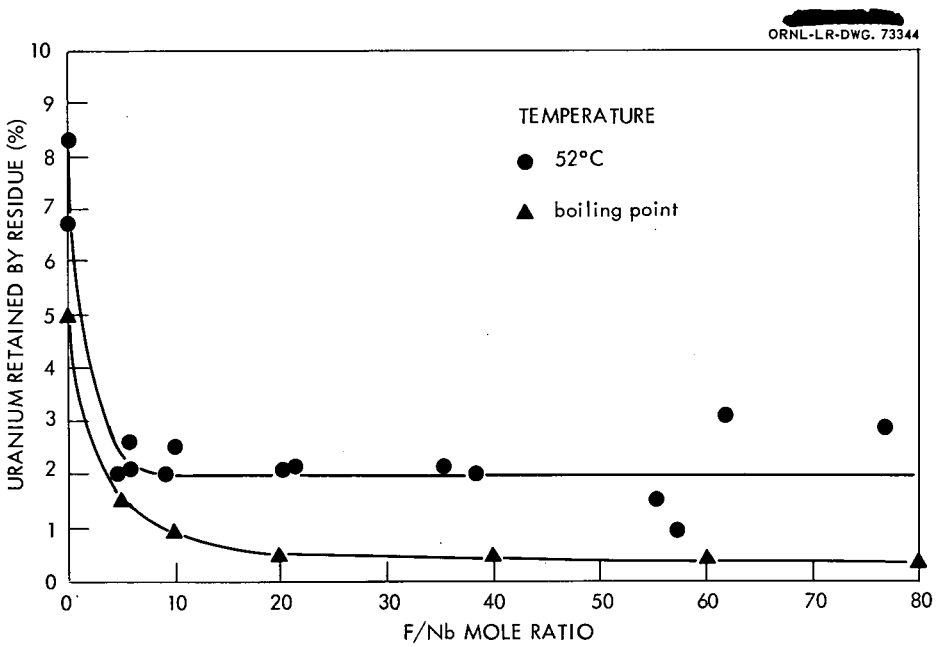


Fig. 6. Effect of temperature on the uranium recovery in $HNO_3$-HF leaching of -8 mesh KIWI-B fuel samples. Boiling point curve is correlation of data shown in Fig. 4.

Table 8. Leaching of -8 Mesh KIWI-B Fuel Samples with $HNO_3$-HF Solutions at 52°C

Conditions: 6-hr leach; residue washed with 3 volumes of water

| Run No. | Fuel Comp. (%) U | Fuel Comp. (%) Nb | Leachant (M) $HNO_3$ | Leachant (M) HF | F/Nb Mole Ratio | Recoveries (%) Solution U | Recoveries (%) Solution Nb | Recoveries (%) Residue U | Recoveries (%) Residue Nb |
|---|---|---|---|---|---|---|---|---|---|
| GL52-1 | 17.6 | 9.2 | 4 | 0 | 0.0 | 91.7 | 0.2 | 8.32 | 99.8 |
| " -8 | 17.5 | 12.6 | 10 | 0 | 0.0 | 93.3 | 0.2 | 6.74 | 99.8 |
| " -2 | 19.7 | 14.2 | 4 | 1.0 | 4.75 | 98.0 | 78.8 | 2.03 | 21.2 |
| " -9 | 17.4 | 12.1 | 10 | 1.0 | 5.59 | 97.4 | 54.6 | 2.64 | 45.4 |
| " -2R | 17.4 | 11.9 | 4 | 1.0 | 5.68 | 97.9 | 82.7 | 2.09 | 17.3 |
| " -3 | 17.9 | 13.9 | 4 | 1.0 | 9.68 | 98.0 | 96.6 | 2.04 | 3.4 |
| " -10 | 17.4 | 13.2 | 10 | 1.0 | 10.2 | 97.5 | 79.9 | 2.51 | 20.1 |
| " -4 | 18.2 | 13.3 | 4 | 1.0 | 20.3 | 97.8 | 99.9 | 2.09 | 0.03 |
| " -11 | 17.2 | 12.6 | 10 | 1.0 | 21.4 | 97.9 | 99.7 | 2.10 | 0.3 |
| " -15 | 17.5 | 13.0 | 4 | 1.0 | 28.6 | 99.2 | 99.6 | 0.77 | 0.04 |
| " -12 | 17.0 | 15.2 | 10 | 1.0 | 35.5 | 97.8 | 99.8 | 2.22 | 0.2 |
| " -5 | 17.6 | 14.2 | 4 | 1.0 | 38.2 | 98.0 | 93.0 | 2.02 | 7.0 |
| " -6 | 21.0 | 14.7 | 4 | 1.0 | 55.2 | 98.5 | 99.3 | 1.49 | 0.71 |
| " -7 | 17.5 | 18.7 | 4 | 1.0 | 57.9 | 99.1 | 98.2 | 0.90 | 1.8 |
| " -13 | 17.6 | 13.1 | 10 | 1.0 | 61.8 | 97.0 | 76.4 | 3.05 | 23.6 |
| " -14 | 17.6 | 14.1 | 10 | 1.0 | 76.7 | 97.1 | 94.2 | 2.89 | 5.8 |

## 4.2 Multiple Leaching

Leaching powdered KIWI-B fuel samples twice for 4 to 6 hr with boiling $HNO_3$-HF solutions resulted in effective removal of the uranium at much lower F/Nb mole ratios than required for the same recovery in a single leach. Recoveries in each leach and subsequent water washes were about those expected on the basis of the actual F/Nb mole ratio for that cycle, assuming that the correlation of uranium loss with F/Nb ratio (Fig. 4) is not affected by variations in the uranium content in the graphite. For example, on leaching 8-20 mesh fuel under conditions where the F/Nb mole ratio is about 3, a uranium loss in the first cycle of about 2% would be expected (Fig. 4), with attendant dissolution of perhaps 25% of the niobium. In a second, duplicate cycle (where the F/Nb mole ratio would be about 4), dissolution of 98.5% of the remaining uranium would be expected. The approximate overall loss would than be 2 x 0.015 = 0.03%. In preliminary experiments, losses from -16 mesh fuel were 0.01 to 0.03% after two successive leaches with boiling 10 M $HNO_3$-0.05 M HF when the overall F/Nb mole ratio was only 2-8 (Table 9). Actually, particle size was not very important; losses were about 0.01% from -200 mesh samples under about the same conditions. Multiple leaching under conditions where the F/Nb mole ratio was about 40 in the first cycle and as high as 2000 in the second resulted in losses of about 0.09% (Table 9). If this procedure is studied further, the major effort should be devoted to minimizing the F/Nb mole ratio in each cycle without impairing the uranium recovery.

## 4.3 Preliminary $HNO_3$ Leach Followed by HF-$HNO_3$ Dissolution of NbC

A variation of the multiple-leach technique involves a preliminary nitric acid leach of the ground fuel to recover most of the uranium, followed by a $HNO_3$-HF digestion to dissolve the NbC liner and recover most of the remaining uranium. This procedure is perhaps the best for KIWI-B fuel but is not applicable to fuels that contain coated fuel particles. In four experiments with -8 mesh KIWI-B fuel, recoveries in each cycle were about those expected on the basis of the F/Nb mole ratio. The uranium loss after a 4-hr digestion with boiling 15.8 M $HNO_3$ (3.5 ml per gram of fuel) and three water washes was about 5% (Table 10). In the second 4-hr cycle

Table 9. Recovery of Uranium by Multiple $HNO_3$ Leaching of Powdered KIWI Fuel Samples

Conditions: Each sample leached twice with indicated reagent; sample washed with 3 vols of water after each leach.

| Run No. MC- | Fuel Type KIWI- | Fuel Comp. (%) | | Mesh Size of Screen Passed | Leachant (M) | | F/Nb Mole Ratio[a] | Time (hr)[b] | Distribution (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | 1st Cycle | | 2nd Cycle | | Residue | |
| | | U | Nb | | $HNO_3$ | HF | | | U | Nb | U | Nb | U | Nb |
| 5 | B | 16.6 | 11.4 | 16 | 10 | 0.5 | 2.0 | 4 | 99.2 | 6.6 | 0.8 | 4.5 | 0.01 | 88.9 |
| 7 | B | 17.9 | 9.9 | 200 | 10 | 0.5 | 2.4 | 4 | 99.0 | 25.9 | 1.0 | 24.1 | 0.01 | 50.0 |
| 6 | A' | 9.8 | 3.8 | 200 | 10 | 0.5 | 6.1 | 4 | 99.5 | 69.7 | 0.2 | 26.9 | 0.30 | 3.4 |
| 4 | A' | 8.8 | 2.8 | 16 | 10 | 0.5 | 8.3 | 4 | 98.5 | 35.4 | 1.5 | 17.5 | 0.03 | 47.1 |
| 1 | B | 17.5 | 15.4 | 8 | 10 | 1.0 | 35.1 | 6 | 99.8 | 97.2 | 0.13 | 2.8 | 0.09 | 0.03 |
| 2 | B | 19.4 | 13.6 | 8 | 10 | 1.0 | 39.6 | 6 | 99.7 | 98.0 | 0.19 | 2.0 | 0.09 | 0.04 |
| 3 | B | 17.6 | 13.3 | 8 | 10 | 1.0 | 40.6 | 6 | 99.8 | 98.3 | 0.10 | 1.7 | 0.09 | 0.02 |

[a] For first leach; overall ratio doubled when second leach is included.

[b] Leaching time for each cycle.

Table 10. $HNO_3$-HF Leaching of -8 Mesh KIWI-B Fuel Specimens after Preliminary 15.8 M $HNO_3$ Leach

Conditions: Sample leached 4 hr with boiling 15.8 M $HNO_3$ (3.5 ml/g) and washed with 3 vol of water; sample then leached with $HNO_3$-HF solution for 4 hr, filtered, and washed with 3 vol of water. 1.5 M $Al(NO_3)_3$ added to filtrate to give Al/F mole ratio of 1 and to precipitate dissolved niobium as hydrous $Nb_2O_5$.

| Run No. | Fuel Comp. (%) | | Leachant (M) | | F/Nb Mole Ratio | Final Distribution (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Prel. Leach | | $HF-HNO_3$ Leach | | $Nb_2O_5$ Ppt. | | Graphite Residue | |
| | U | Nb | $HNO_3$ | HF | | U | Nb | U | Nb | U | Nb | U | Nb |
| GL-6 | 17.5 | 14.0 | 1 | 1 | 3 | 96.4 | 0.03 | 3.42 | 0.44 | 0.12 | 35.6 | 0.007 | 63.9 |
| GL-7 | 17.1 | 15.7 | 1 | 1 | 5 | 92.2 | 0.03 | 7.56 | 7.97 | 0.28 | 56.9 | 0.016 | 35.1 |
| GL-8 | 17.0 | 15.1 | 1 | 3 | 3 | 96.2 | 0.21 | 3.62 | 0.43 | 0.18 | 19.2 | 0.060 | 80.7 |
| GL-9 | 18.6 | 13.0 | 1 | 3 | 5 | 95.1 | 0.04 | 4.19 | 4.47 | 0.35 | 78.8 | 0.34 | 16.7 |

with 1 M $HNO_3$ containing either 1 or 3 M HF (F/Nb mole ratios of 3 and 5), about 99% of the remaining uranium was recovered. The overall uranium losses to the graphite residue were generally less than 0.1% (Table 10). From the data given in Fig. 4, the loss expected, using an average F/Nb mole ratio of 4, would be 5 x 0.018 = 0.09%.

In an optional step, after removal of the $HNO_3$-HF solution by filtration, 1.5 M $Al(NO_3)_3$ was added to the filtrate such that the Al/F mole ratio was unity. Most of the dissolved niobium was precipitated by addition of the aluminum nitrate. The hydrous niobic oxide precipitate carried 0.1 to 0.4% of the uranium (Table 10).

### 4.4 Addition of Aluminum Nitrate to Leach Solutions

Niobium can be precipitated from the product solutions by the addition of aluminum nitrate. Fluoride ion in the solutions is complexed by the aluminum. Two potential processing techniques based on these principles were briefly investigated: (1) "internal" addition of aluminum nitrate, wherein the $Al(NO_3)_3$ was added to the leach liquor-graphite slurry prior to filtration, and (2) "external" addition, wherein the aluminum nitrate was added to the filtrates after washing of the graphite residue. Precipitation of the niobium was nearly quantitative in both methods, but, since the resultant slurries and slimy niobic oxide precipitates were extremely difficult to filter, final evaluation of these methods must await studies involving other solid-liquid separation methods such as centrifugation.

#### 4.4.1 "Internal" $Al(NO_3)_3$ Addition

The chief potential advantage of the "internal" aluminum-addition procedure is that the niobium would be left in the graphite residue and would be discharged to waste with it. Leaching for 6 or 20 hr with boiling 4 or 10 M $HNO_3$ containing 0.3 or 0.5 M HF followed by addition of $Al(NO_3)_3$ to give an Al/F mole ratio of 1 resulted in uranium recoveries of at least 99% when the F/Nb mole ratio was greater than about 3.5, although at least 95% of the niobium remained in the residue (Table 11). Filtration and washing of the residue was extremely slow due to the slimy nature of the precipitated niobic oxide. Since filtration is not practical, centrifugation or direct solvent extraction from the slurry should be studied.

Table 11. $HNO_3$-HF Leaching and "Internal" $Al(NO_3)_3$ Addition Experiments with -8 Mesh KIWI-B Fuel Samples

Conditions given in the text

| Run No. | Fuel Comp. (%) U | Fuel Comp. (%) Nb | Leachant (M) $HNO_3$ | Leachant (M) HF | F/Nb Mole Ratio | Leaching Time[a] (hr) | Amount in Residue (%) U | Amount in Residue (%) Nb |
|---|---|---|---|---|---|---|---|---|
| GL-17 | 17.5 | 16.3 | 10 | 0.3 | 2.2 | 6 | 1.31 | 99.4 |
| GL-16 | 17.1 | 16.2 | 10 | 0.3 | 3.8 | 6 | 0.95 | 99.0 |
| GL-2 | 18.6 | 11.0 | 4 | 0.5 | 3 | 6 | 1.48 | 98.1 |
| GL-I20 | 17.0 | 20.5 | 4 | 0.5 | 3 | 20 | 1.80 | 99.2 |
| GL-1 | 19.0 | 13.1 | 4 | 0.5 | 5 | 6 | 0.75 | 97.0 |
| GL-5 | 18.8 | 11.6 | 10 | 0.5 | 3 | 6 | 1.12 | 98.1 |
| GL-IV20 | 16.6 | 16.3 | 10 | 0.5 | 3.7 | 20 | 0.76 | 98.0 |
| GL-4 | 19.7 | 10.1 | 10 | 0.5 | 5 | 6 | 0.89 | 95.4 |
| GL-22 | 19.3 | 13.0 | 10 | 0.5 | 5 | 6[b] | 0.48 | 98.9 |

[a] Leaching time in $HNO_3$-HF only; sample leached an additional hour after $Al(NO_3)_3$ addition.

[b] Digestion was continued for an additional 16 hr after addition of aluminum nitrate.

The experiments were conducted in the following manner: -8 mesh KIWI-B fuel samples were digested in the $HNO_3$-HF leachant for either 6 or 20 hr. After the leach, 1.5 M $Al(NO_3)_3$ was added to give an Al/F mole ratio of 1, and digestion was continued for an additional hour (except in run 22 where the digestion was continued for 16 hr). The product solution was removed by vacuum filtration, and the residue was washed with 3 volumes of cold water prior to analysis.

### 4.4.2 "External" $Al(NO_3)_3$ Addition

Addition of the aluminum nitrate to the filtrates after leaching -8 mesh KIWI-B fuel with boiling 4 or 10 M $HNO_3$ containing 0.3-0.5 M HF resulted in the precipitation of most of the niobium that had been dissolved. This precipitate carried at most 0.25% of the uranium (Table 12). The experiments were conducted in the same general manner as those involving the "internal" addition of aluminum nitrate. Filtration of the niobic oxide

Table 12. $HNO_3$-HF Leaching and "External" $Al(NO_3)_3$ Addition Experiments with -8 Mesh KIWI-B Fuel Samples

Conditions given in the text

| Run No. | Fuel Comp. (%) | | Leachant (M) | | F/Nb Mole Ratio | Distribution (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Solution[a] | | Ppt | | Residue | |
| | U | Nb | $HNO_3$ | HF | | U | Nb | U | Nb | U | Nb |
| GL-13 | 16.7 | 15.9 | 4 | 0.3 | 2.3 | 98.3 | 6.2 | 0.02 | | 1.67 | 93.8 |
| GL-12 | 20.0 | 13.5 | 4 | 0.3 | 5 | 99.3 | 50.8 | | | 0.74 | 49.2 |
| GL-11 | 18.9 | 10.2 | 10 | 0.3 | 3 | 99.3 | 14.5 | 0.004 | | 0.73 | 85.5 |
| GL-10 | 20.4 | 10.3 | 10 | 0.3 | 5 | 99.5 | 65.3 | 0.005 | | 0.47 | 34.7 |
| GL-21 | 20.7 | 16.5 | 4 | 0.5 | 2.2 | 97.6 | 6.3 | 0.20 | 15.1 | 2.23 | 78.6 |
| GL-20 | 22.4 | 16.9 | 4 | 0.5 | 3.6 | 98.6 | 9.4 | 0.24 | 19.5 | 1.16 | 71.1 |
| GL-19 | 22.5 | 16.5 | 10 | 0.5 | 2.2 | 99.1 | 3.4 | 0.045 | 1.7 | 0.89 | 94.9 |
| GL-18 | 20.2 | 12.5 | 10 | 0.5 | 5 | 99.4 | 20.7 | 0.002 | 0.9 | 0.63 | 78.4 |

[a] Virtually all the aluminum remained in solution. In most cases, 1 mole of fluoride remained in the graphite residue for each mole of niobium present there, presumably as $NbO_2F$.

precipitate was very difficult. At least 99% of the uranium was recovered when the F/Nb ratio was 3.5 or greater (Table 12). At least 35% of the niobium remained in the graphite residue, reflecting again the ineffiency of dissolution when the F/Nb mole ratio is less than about 15 (Sec. 4.1).

The amorphous (to x rays), precipitate of niobic oxide (presumably $3\ Nb_2O_5 \cdot 7H_2O$) obtained from $HNO_3$-HF solutions containing $UO_2^{2+}$ and $NbOF_5^{2-}$ ions on addition of aluminum nitrate carried almost no uranium or aluminum. Sorption, rather than compound formation, is therefore the probable mechanism by which traces of these impurities become associated with the precipitate. The amounts sorbed increased with the amount of precipitate formed. Ionic analyses on typical precipitates of this type showed that the niobium content was 52 to 59%, compared with the theoretical of 60% for the hydrated oxide mentioned above.

## 4.5 Solution Stability

The conditions required for attaining stable $HNO_3$-HF solutions containing niobium from the processes described in this report have not yet been fully evaluated. Generally, product solutions (hydrogen ion concentrations of 1 to 6 N) were stable at room temperature when the F/Nb mole ratio was greater than 25, but precipitates were formed in some solutions where this ratio was higher. Since knowledge of solution stability is vital to complete development of aqueous methods for processing Rover fuels, it is being studied intensively and will be reported separately.

The oxyfluoride $NbO_2F \cdot 1/2\ H_2O$ was the solid precipitated most frequently, although some evidence was found for the existence of $NbOF_3$. At equilibrium at 25°C, only about 5 moles of fluoride ion (in HF and HF-$HNO_3$ solutions) are necessary to solubilize 1 mole of niobium starting with either $Nb_2O_5$ or $NbO_2F \cdot 1/2\ H_2O$[24]. The resulting solutions are stable. These results are in agreement with those of Russian workers who measured the solubility of $Nb_2O_5$ in HF solutions[25]. At room temperature, the rate at which $NbO_2F \cdot 1/2\ H_2O$ dissolves in $HNO_3$-HF solutions is extremely slow. The probable reactions are:

$$2\ NbO_2F \cdot 1/2\ H_2O_{(s)} \longrightarrow Nb_2O_{5(s)} + 2\ HF_{(aq)} \qquad (1)$$

$$Nb_2O_{5(s)} + 10\ HF_{(aq)} \longrightarrow 2NbOF_5^{2-} + 4H^+ + 3H_2O \qquad (2)$$

Reaction (1) requires nearly a year for attainment of equilibrium at room temperature, starting with freshly precipitated oxyfluoride[24], whereas reaction (2) requires only about 2 days[24,25]. Apparently, when wash water was added to the hot process solutions the oxyfluoride that was formed by hydrolysis precipitated and only very slowly redissolved at room temperature in $HNO_3$-HF solutions where the F/Nb mole ratio is less than about 25. Either the hydrolysis is suppressed or the rate of redissolution is very rapid in solutions where the F/Nb mole ratio is higher. These generalized conclusions suggest that perhaps a low-temperature process would be effective in avoiding the severe hydrolysis that occurs in boiling solutions and would permit use of much lower F/Nb mole ratios in solubilizing the niobium.

## 5.0 MODIFIED 90%-$HNO_3$ PROCESS

The 90%-$HNO_3$ process involves the simultaneous disintegration and leaching of graphite-base fuels in 18 to 24 M $HNO_3$ at temperatures from 25°C to the boiling point[9,10,12]. However, the method is not applicable to fuels containing coated fuel particles, and, with all KIWI fuels, hydrofluoric acid must be added to the nitric acid to dissolve the NbC liner. With KIWI-B fuels, which contained NbC but no coated fuel particles, uranium recoveries of about 99.6% were achieved in a single disintegration-leach with boiling 90 to 95% $HNO_3$ containing 0.5-2 M HF, if the F/Nb mole ratio was at least 20. The powdered residue was washed with three volumes of water after the leach to ensure recovery of all uranium solubilized. Multiple leaching was also briefly studied.

### 5.1 Disintegration-Leaching in $HNO_3$-HF

KIWI-B fuel specimens were disintegrated and leached in 90 to 95% $HNO_3$ containing 0.5-2 M HF (F/Nb mole ratios of 0 to 26) both at room temperature and at the boiling point. The only variables that affected the uranium recovery were the F/Nb mole ratio and the temperature. In boiling solutions, uranium losses to the graphite residue decreased from about 3 to 0.4% as the F/Nb mole ratio increased from 0 to 36 (Fig. 7 and Table 13). Disintegration-leaching at room temperature was not very effective; uranium

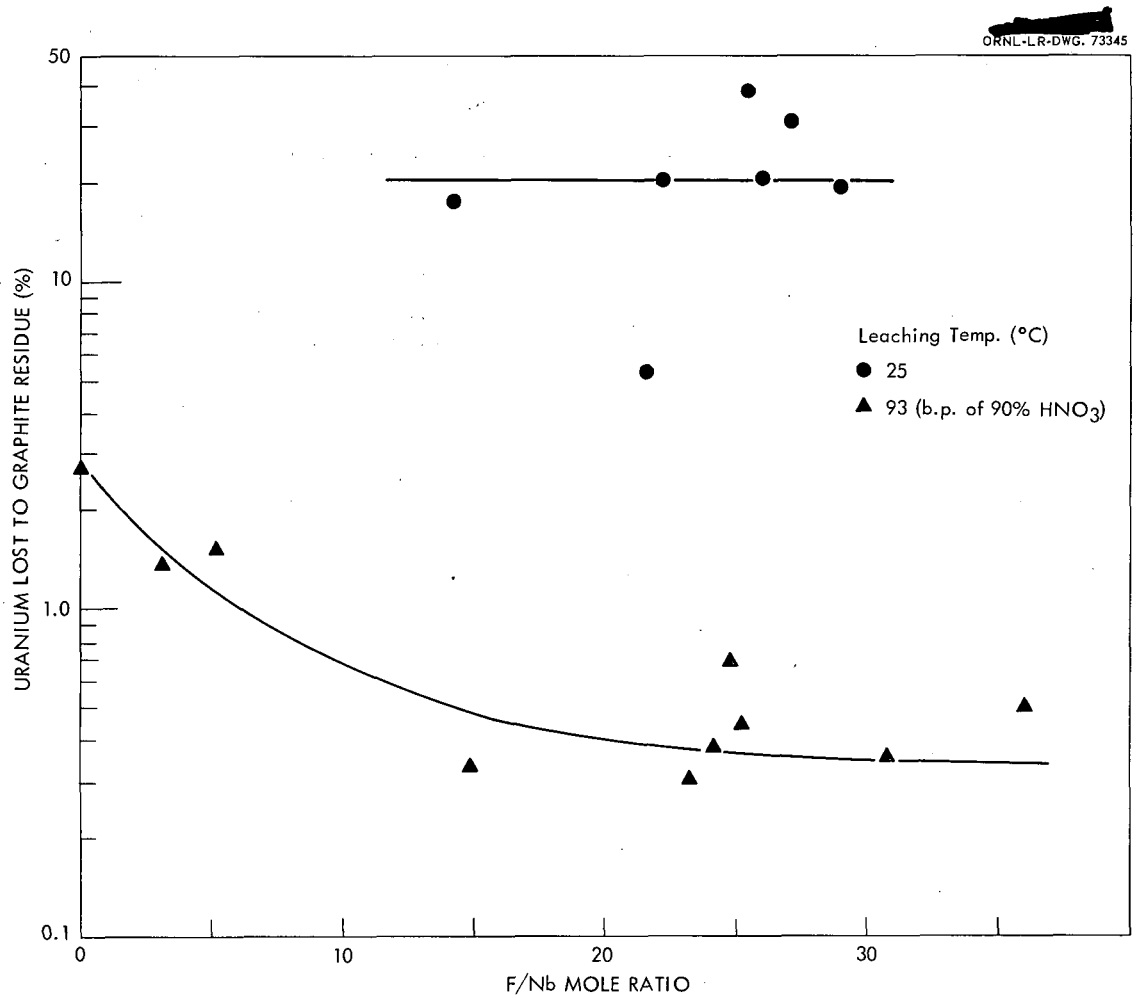


Fig. 7. Effect of F/Nb mole ratio on the recovery of uranium from KIWI-B fuel specimens in simultaneous disintegration and leaching with 90 to 95% $HNO_3$ containing 0.5-2 M HF.

losses to the residue were generally around 20% (Fig. 7). In the experiments with boiling reagents, most of the niobium remained with the graphite residue, probably as a hydrolysis product such as $NbO_2F \cdot 1/2\ H_2O$ (Table 13). On the other hand, in the experiments at room temperature (where hydrolysis would be less severe) most of the niobium was found in the product solution. Experiments were conducted by disintegrating and leaching fuel specimens for 6 hr, removing the solution by vacuum filtration, and washing the residue with three volumes of cold water. Filtration of the residue was relatively easy, compared with filtration of mechanically-ground fuel (see Sec. 4.1.2). This ease of filtration and

Table 13. Recovery of Uranium from KIWI-B Fuel by Simultaneous Disintegration and Leaching with 90-95% $HNO_3$ Containing HF

Conditions: 6-hr disintegration-leach followed by washing with 3 vol of cold water.

| Run No. | Fuel Comp. (%) U | Fuel Comp. (%) Nb | Acid Conc. (M) $HNO_3$ | Acid Conc. (M) HF | F/Nb Mole Ratio | Temp. (°C) | Amount Remaining in Residue (%) U | Amount Remaining in Residue (%) Nb |
|---|---|---|---|---|---|---|---|---|
| FN-B | 16.5 | 15.2 | 23[a] | 0 | 0 | 88[c] | 2.70 | 99.9 |
| FN-1 | 19.5 | 18.9 | 21[b] | 0.5 | 3.2 | 93[d] | 1.39 | 55.4 |
| FN-5 | 18.0 | 12.2 | 21 | 1.0 | 5.2 | 93 | 1.52 | 85.2 |
| FN-4R | 16.9 | 13.6 | 21 | 1.0 | 14.8 | 93 | 0.33 | 93.4 |
| FN-3 | 17.2 | 12.9 | 21 | 0.5 | 23.2 | 93 | 0.30 | 93.3 |
| FN-4 | 19.1 | 12.4 | 21 | 1.0 | 24.2 | 93 | 0.38 | 0.6 |
| FN-8 | 17.4 | 10.8 | 23 | 1.0 | 24.8 | 88 | 0.69 | 96.0 |
| FN-9 | 18.1 | 10.7 | 23 | 2.0 | 25.2 | 88 | 0.44 | 93.5 |
| FN-6 | 17.8 | 13.2 | 21 | 1.0 | 30.7 | 93 | 0.35 | 85.4 |
| FN-7 | 18.0 | 7.5 | 21 | 2.0 | 36.1 | 93 | 0.50 | 54.6 |
| FN-4CR | 18.5 | 14.2 | 21 | 1.0 | 14.3 | 25 | 17.7 | 21.6 |
| FN-3C | 21.0 | 13.9 | 21 | 0.5 | 21.6 | 25 | 5.2 | 18.0 |
| FN-4C | 18.5 | 13.5 | 21 | 1.0 | 22.2 | 25 | 20.3 | 8.2 |
| FN-7C | 17.3 | 10.6 | 21 | 2.0 | 25.4 | 25 | 38.1 | 2.5 |
| FN-8C | 16.2 | 10.4 | 23 | 1.0 | 26.0 | 25 | 21.0 | 4.4 |
| FN-9C | 17.8 | 9.9 | 23 | 2.0 | 27.2 | 25 | 30.6 | 4.1 |
| FN-6C | 19.0 | 13.9 | 21 | 1.0 | 29.0 | 25 | 19.3 | 1.2 |

[a] 95% $HNO_3$ is about 23 M.

[b] 90% $HNO_3$ is about 21 M.

[c] The boiling point of 95% $HNO_3$ is about 88°C.

[d] The boiling point of 90% $HNO_3$ is about 93°C.

the high uranium recoveries perhaps make the 90%-$HNO_3$ process the best aqueous method for processing KIWI fuel which does not contain coated fuel particles. Corrosion tests indicated that aluminum might serve as a material of construction for boiling 90% $HNO_3$ containing HF;[18,22,23,28] however, if corrosion of metals by the diluted product is too severe, plastic-lined solvent extraction equipment might be required.

### 5.2 Disintegration in 90% $HNO_3$ Followed by $HNO_3$-HF Leaching

This variation of the 90%-$HNO_3$ process involves preliminary disintegration in the nitric acid (usually requiring about 4 hr) followed by the

addition of HF and further digestion (about 3 hr) to effect recovery of the uranium associated with the NbC liner. The graphite residue is washed at this point and the cycle repeated. As expected, the recoveries were related to the F/Nb mole ratio; in the two cycles, the amount of uranium lost to the residue decreased from about 3.9 to 0.05% as the total F/Nb mole ratio increased from 0 to 6 (Table 14). The low losses obtained by multiple leaching at low F/Nb mole ratios were not surprising in light of similar grind-leach experiments (Sec. 4.2). The geometric mean particle size of the graphite residue was 520 to 730 μ (Table 14).

## 6.0 ELECTRODISINTEGRATION

Graphite-base fuels are readily disintegrated when made anodes in an electrolyte such as nitric acid[10,26,27]. With fuels which do not contain coated fuel particles, dissolution of the uranium occurs simultaneously with the disintegration. However, when a KIWI-A' specimen containing 7.8% uranium and 3.3% niobium was anodically disintegrated (about 1 amp/cm$^2$) in 15.8 M $HNO_3$ for 4 hr at 93°C and the residue water-washed, the uranium recovery was relatively low:

| | Electrolyte (%) | Residue (%) |
|---|---|---|
| Uranium | 97.6 | 2.45 |
| Niobium | 0.12 | 99.9 |

This result is not surprising since pure NbC was not affected when electrolytically anodized in 3 and 15.8 M $HNO_3$ at 93°C (current density, about 1 amp/cm$^2$). NbC might be a suitable anode material for electrolytic processes. These results point out again that some uranium is associated with the NbC liner and that recovery can be complete only if the liner is dissolved. Anodic dissolution of NbC in $HNO_3$-HF solutions might be effective. However, even though the liner problem were solved, electrolytic methods do not appear attractive for future Rover fuels which will contain carbon-coated fuel particles[10,27]. The graphite matrix is readily disintegrated but the particle coatings remain virtually intact.

## 7.0 DISSOLUTION OF NbC

Scouting studies[9] indicated that NbC is best dissolved in boiling $HNO_3$-HF solutions. It would be desirable to add aluminum nitrate to such

Table 14. Disintegration of KIWI-B Fuel in Boiling 90% $HNO_3$ Followed by Leaching in $HNO_3$-HF Solutions

Sample disintegrated in 4 hr in boiling 90% $HNO_3$; HF solution added; fuel digested for additional 3 hr before filtering and water-washing, then cycle was repeated

| Run No. | Fuel Comp. (%) | | Leachant Conc[a] (M) | | Total F/Nb Mole Ratio | Distribution (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | First Leach And Washes | | Second Leach And Washes | | Residue | |
| | U | Nb | $HNO_3$ | HF | | U | Nb | U | Nb | U | Nb |
| SL-6 | 17.8 | 13.1 | 21 | 0.0 | 0 | 94.8 | 0.25 | 1.31 | 0.05 | 3.89 | 99.7 |
| SL-5 | 16.8 | 12.3 | 14 | 0.1 | 0.54 | 96.6 | 0.27 | 1.43 | 0.14 | 2.00 | 99.6 |
| SL-9 | 17.9 | 12.4 | 10 | 0.1 | 1.0 | 97.0 | 2.89 | 1.27 | 1.85 | 1.70 | 95.3 |
| SL-4 | 16.9 | 11.5 | 14 | 0.5 | 2.8 | 96.8 | 1.2 | 2.06 | 1.7 | 1.15 | 97.1 |
| SL-7 | 17.7 | 9.4 | 10 | 0.3 | 4.2 | 96.4 | 4.47 | 3.07 | 17.8 | 0.58 | 77.8 |
| SL-A | 17.3 | 10.8 | 10 | 0.5 | 6.0 | 98.6 | 23.8 | 1.30 | 0.03 | 0.05 | 76.2 |

[a] Concentration after diluting the original 90% $HNO_3$ (21 M) with the appropriate HF solution.

solutions to inhibit corrosion of metallic containers. This does not appear feasible, however, since the addition of only a small amount of aluminum nitrate to the dissolvent drastically reduces the rate of dissolution of NbC as

| Run No. | $Al(NO_3)_3$ Conc. (M) | Amt. of NbC Dissolved (%) |
|---|---|---|
| 1 | 0.0 | 27.3 |
| 2 | 0.25 | 0.46 |
| 3 | 0.50 | 0.076 |
| 4 | 0.75 | 0.071 |

These 0.5-hr tests were made by allowing 0.7- to 1-g specimens of pure NbC to react with boiling 10 M $HNO_3$-0.5 M HF containing $Al(NO_3)_3$. Although NbC is virtually unaffected by boiling concentrated HF, it can be dissolved in HF to which $H_2O_2$ is added incrementally:

| Run No. | Init. Diss. Rate (%/hr) | HF Conc. (M) Initial | HF Conc. (M) Final | $H_2O_2$ Added |
|---|---|---|---|---|
| 1 | 0.17 | 28 | 28 | No |
| 2 | 0.84 | 14 | 7 | Yes |
| 3 | 1.7 | 28 | 14 | Yes |

An initial rate of 2%/hr is roughly equivalent to a linear penetration rate of 0.5 mg $min^{-1}$ $cm^{-2}$.

Another potential dissolvent for NbC is nitric acid to which $H_2O_2$ is added continuously. In 40-min tests with intermittent addition of 30% $H_2O_2$ the average dissolution rate decreased with increasing $HNO_3$ concentration:

| Run No. | $HNO_3$ Conc. (M) | Avg. Rate (%/hr) |
|---|---|---|
| NC-5 | 3 | 1.97 |
| NC-4 | 4 | 0.78 |
| NC-3 | 8 | 0.69 |
| NC-6 | 10 | 0.93 |
| NC-2 | 16 | Wt. gain (0.35%) |

The proportionately higher rates obtained in runs NC-5 and -6 may be the result of having used fresh NbC specimens. The buttons used in the other experiments had previously been contacted with $HNO_3$-HF solutions, and their appearance suggested the presence of a surface film. In any event, the use of $HNO_3$-$H_2O_2$ or HF-$H_2O_2$ as dissolvents for NbC would depend on the

successful addition of the peroxide to the boiling solutions, which may be difficult on an engineering scale.

## 8.0 CORROSION STUDIES

Corrosion in $HNO_3$-HF solutions is being studied in an effort to find a metallic material suitable for the construction of a dissolver for the aqueous processes being developed for the recovery of uranium from Rover fuel by W. E. Clark and L. Rice[28]. Aluminum and type 347 stainless steel were the most promising materials tested in boiling $HNO_3$ (14 to 23 M) containing up to 3 M HF (Table 15). With type 6061 aluminum, the corrosion rate in solution decreased from about 5 mils/month to less than 0.1 mil/month as the nitric acid concentration increased from 14 to 22 M. Below 14 M $HNO_3$, corrosion increased. When the nitric acid concentration was greater than 14 M, aluminum was almost completely passivated by 1 M HF, and activation of the metal did not occur in the presence of graphite and uranium, as was the case with type 309 SCb stainless steel.

In tests with Corronel 230, the corrosion rate varied from about 2 mils/month in boiling 4 M $HNO_3$-0.3 M HF to complete dissolution in 1 M $HNO_3$-3 M HF[28]. The corrosion rate was markedly lower at 60°C, and dilute acid processes operated below this temperature should be considered.

Table 15. Corrosion of Aluminum and Stainless Steel in Boiling $HNO_3$-HF Solutions

| Alloy | Solution (M) | | Exposure Time (hr) | Corrosion Rate (mils/month) | | |
|---|---|---|---|---|---|---|
| | $HNO_3$ | HF | | Vapor | Interface | Solution |
| 309 SCb SS | 23 | 1 | 24 | <0.1 | 0.6 | 0.3 |
| | 23 | 1 | 144 | <0.1 | 0.6 | 0.3 |
| 347 SS | 22 | 2 | 24 | <0.1 | 0.4 | 0.4 |
| | 22 | 2 | 96 | 0.1 | 0.5 | 0.5 |
| 6061 Al | 14 | 1 | 24 | gain | gain | gain |
| | 14 | 1 | 96 | 0.5 | gain | 1.0 |
| | 14 | 2 | 24 | 2.6 | <0.1 | 1.7 |
| | 14 | 2 | 96 | 3.5 | 1.7 | 3.2 |
| | 14 | 3 | 24 | 5.0 | 2.1 | 5.4 |
| | 14 | 3 | 96 | 4.7 | 2.5 | 4.0 |
| | 15.6 | 2 | 24 | gain | gain | gain |
| | 15.6 | 2 | 96 | <0.1 | 0.3 | 0.6 |
| | 18 | 1 | 96 | 0.3 | 0.1 | <0.1 |
| | 18 | 5 | 96 | 0.3 | 0.1 | <0.1 |
| | 20 | 1 | 96 | 0.1 | <0.1 | <0.1 |
| | 22 | 2 | 72 | 0.2 | gain | gain |
| | 23 | 1 | 24 | <0.1 | gain | gain |

## 9.0 REFERENCES


1. Quarterly Status Report of LASL Rover Program for Period Ending Sept. 20, 1960, LAMS-2472 (Oct. 31, 1960).

2. Ibid, for Period Ending Dec. 20, 1960, LAMS-2505 (Jan. 31, 1961).

3. Ibid, for Period Ending March 20, 1961, LAMS-2545 (April 28, 1961).

4. Ibid, for Period Ending Dec. 20, 1961, LAMS-2659 (Jan. 26, 1962).

5. Personal communication, R. D. Baker, LASL, to R. E. Brooksbank, ORNL, May 29, 1962. (see also R. E. Brooksbank, Rover Program - Trip to LASL, May 29, 1962, ORNL-CF-62-6-27 (June 15, 1962).

6. A. Fitch, Jr., "Reprocessing of Rover and Pluto Fuels: Interim Progress Report," ORNL-2514 (May 2, 1958).

7. A. Fitch, Jr. and L. M. Ferris, "A Tentative Grind-Leach Process for Rover Fuels," ORNL-2640 (Dec. 26, 1958).

8. M. J. Bradley and L. M. Ferris, "Reprocessing of Rover Fuel: Laboratory Development Progress to April 1, 1959," ORNL-2741 (Oct. 19, 1959).

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

10. L. M. Ferris, A. H. Kibbey, M. J. Bradley, "Processes for Recovery of Uranium and Thorium from Graphite-base Fuel Elements. Part II," ORNL-3186 (Nov. 16, 1961).

11. M. J. Bradley and L. M. Ferris, Nucl. Sci. and Eng. 8, 432 (1960).

12. M. J. Bradley and L. M. Ferris, Ind. Eng. Chem., 53, 279 (1961).

13. J. Binford, "Kinetics of the Oxidation of Graphite," p. 38 in Literature of the Combustion of Petroleum, Advances in Chemistry Series, No. 20, American Chemical Society, Washington, 1958.

14. P. L. Walker, Jr., F. Rusinko, Jr., and L. G. Austin, "Gas Reactions in Carbon," p. 203 in Advances in Catalysis, Vol. XI, Academic Press, New York, 1959.

15. J. W. Prados, Nuclear Safety 2 (4),8(June, 1961)

16. G. L. Miller, p. 613 Tantalum and Niobium, Academic Press, New York, 1959.

17. D. G. Reid, C. E. Stevenson, R. B. Lemon, and F. K. Wrigley, "Zirconium Alloy Fuel Processing," Proc. 2nd Internat'l Conf. Peaceful Uses Atomic Energy, Geneva, 1958. P/526, Vol 17, p. 145.

18. F. L. Culler, Jr., Rover Report for April 1962, ORNL-TM-227 (May 15, 1962).

19. J. E. Day, Ind. Eng. Chem. 28, 236 (1936).

20. G. J. Nebel and P. L. Cramer, ibid., 47, 2394 (1955).

21. F. L. Culler, Jr., "Rover Report for May 1962," ORNL-TM-267 (July 3, 1962).

22. Ibid, for March 1962, ORNL-TM-199 (April 19, 1962).

23. W. K. Boyd and E. L. White, "Compatibility of Rocket Propellants with Materials of Construction," DMIC-Memo-65 (Sept. 15, 1960).

24. L. M. Ferris, ORNL, unpublished data.

25. N. S. Nikolaev and Yu. A. Buslaev, Russ. J. Inorg. Chem. (Eng. Trans.), 4, 84 (1959).

26. L. M. Fromm, "Recovery of Uranium from Graphite Shapes by Electrolytic Disintegration in Nitric Acid," ORNL-238 (Feb. 24, 1949).

27. R. A. Ewing, T. S. Elleman, and R. B. Price, Trans. Am. Nuclear Soc., 4 (1), 152 (1961).

28. R. E. Blanco, "Progress for Chemical Development Section B for Period Jan. 1-July 1, 1962," ORNL-TM-377 (in press).

[redacted]



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