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URANIUM RECOVERY FROM KIWI FUEL
ELEMENTS: LABORATORY DEVELOPMENT

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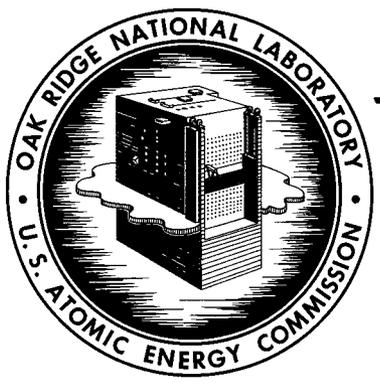
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ABSTRACT

Potential methods for recovering uranium from the graphite-base KIWI reactor fuel elements are being developed at ORNL on a laboratory scale. Three techniques that are being evaluated are: (1) a 90% HNO_3 process, in which the elements are simultaneously disintegrated and leached with 21 M HNO_3 ; (2) a combustion-dissolution process in which the elements are burned in oxygen prior to dissolution of the oxide residue in nitric acid; and (3) a grind-leach process in which the fuels are mechanically ground to a fine powder before being leached with 15.8 M (70%) HNO_3 . Uranium recovery from KIWI-A fuel (a homogeneous dispersion of UC_2 in graphite) is nearly quantitative by either the 90% HNO_3 or combustion-dissolution process. After two 4-hr leaches of irradiated KIWI-A fuel (0.001% burnup) with boiling 90% HNO_3 , the uranium loss to the graphite residue was generally less than 0.5%; about 50% of the long-lived fission products also remained with the residue. The oxide combustion residue could be dissolved completely in boiling 7.5 M HNO_3 -0.75 M HCl . Hydrochloric acid was a necessary component of the dissolvent because of the iron impurity in the fuel. During the combustion, up to 95% of the Ru-106 was volatilized. Uranium can be recovered from NbC-coated KIWI fuels by a modified 90% HNO_3 process in which the NbC is dissolved in HNO_3 -HF solution.

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1.0 INTRODUCTION

In this report are summarized laboratory studies devoted to the development of processing methods for KIWI reactor fuel elements prior to Sept. 1, 1961. The KIWI reactors are prototype rocket engines being developed and tested at Los Alamos Scientific Laboratory (LASL) under the Rover program. Fuel elements for these reactors are dispersions of uranium carbide in graphite (1-3); the uranium content of the elements varies from 2 to 20%. Hydrogen, containing a trace of methane, is used as the propellant-coolant. The first reactor in the series, KIWI-A, tested in July 1959, contained plate fuel elements (1,4). KIWI-A' and KIWI-A3, tested July 8 and Oct. 19, 1960, respectively, contained tubular graphite fuel elements with the propellant-coolant channels coated with NbC to prevent corrosion (2,3). The tubes were about 3/4 in. dia with four 3/16-in.-dia fuel channels per tube. Fuel elements for the KIWI-B series of tests will be similar in composition to those used in the A-series. However, each element will contain seven NbC-coated coolant channels. Six KIWI-B reactor tests are anticipated between July 1961 and July 1962 (3).

A systematic study of processing methods for graphite-base reactor fuels, including the KIWI series, is in progress at ORNL (5). Although the primary objective of these studies is the evolution of practicable methods for the recovery of uranium and thorium from spent fuels by conventional tributyl phosphate-nitric acid solvent extraction methods, the techniques under consideration are equally applicable to recovery from unirradiated scrap. Early studies at ORNL showed that a grind-leach method was feasible for the recovery of uranium from prototype KIWI-A fuel elements (6,7). Since the uranium recoveries were generally lower than desired, particularly from elements containing <5% uranium, a better method, viz., disintegrating and leaching the elements with 90% HNO₃, was developed (8). A third method, combustion of the elements in oxygen followed by dissolution of the ash in nitric acid, has also received cursory investigation (5).

This report contains the results of 90% HNO₃ and combustion-dissolution flowsheet demonstration experiments with actual irradiated KIWI-A fuel specimens and studies of the 90% HNO₃, grind-leach, and combustion-dissolution

processes with unirradiated specimens of the other KIWI reactor fuels. Preliminary data on the dissolution of NbC in HNO_3 -HF solutions are also given.

The chief remaining chemical problem is determining the best method for dissolving the NbC coating without excessively corroding the dissolver vessel. In effect, this means dissolution in solutions of low fluoride ion concentration. More precise determination of the solubility of NbO_2F in HNO_3 -HF solutions will also be required to aid in the choice of process conditions, since the solubility of this compound appears to be affected markedly by the acid concentration. Future studies should also include determination of the stoichiometry of the reaction between NbC and HNO_3 -HF solutions, with emphasis on the off-gas composition; evaluation of potential problems arising from the reactions of uranium carbide and graphite with nitric acid; and corrosion tests with the optimum reagents once they have been chosen.

The authors wish to thank J. W. Ullmann, ORNL Chemical Technology Division, for his aid in procuring the fuel specimens and outlining the experiments with the irradiated specimens. Radiochemical, chemical, and x-ray analyses were provided by the ORNL Analytical Chemistry Division under the direction of G. R. Leddicotte, L. C. Bate, G. R. Wilson, W. R. Laing, R. L. Sherman, and M. M. Murray.

2.0 90% HNO_3 PROCESS

2.1 Flowsheet

The 90% HNO_3 process (8) involves simultaneous disintegration and leaching of the fuel elements with 90% (21.2 M) HNO_3 at temperatures of 25 to 93°C, the boiling point. In the first step of the flowsheet, the fuel is disintegrated and leached (3.5 ml of acid per gram of fuel) over a 4-hr period. The leach liquor is removed by vacuum filtration and the powdered graphite residue is washed three times with water. After removal of the washes by vacuum filtration, the fuel is leached again for 4 hr with a fresh volume of 90% HNO_3 before a final water wash. The leach solutions (about 20 M HNO_3 containing 1-15 g of uranium per liter) can be boiled down separately from the washes

before solvent extraction to allow recycle of 21 M acid. The alternative is to combine the leach and wash solutions prior to the feed adjustment step (boildown) and discard the condensate. Although the disintegration and leaching reaction has not yet been studied completely, preliminary work (5) indicated that the off-gas consisted mainly of NO_2 and CO_2 . No hydrogen was detected.

2.2 KIWI-A Fuel

Uranium Recoveries. Uranium recoveries, as expected from prior work (5,8), were dependent on the uranium content of the specimen, the leaching temperature, and the reaction time. Several irradiated fuel plates (~0.001% burnup) from the KIWI-A test were available for these studies. Plates 4G1 and 3H18, containing about 3 and 12% uranium, respectively, were used in the experiments. Most experiments were conducted under flowsheet conditions; a few samples were leached twice for 24 hr instead of the usual 4 hr.

With 4G1 specimens (containing about 3% uranium), losses to the graphite residue after two 4-hr leaches with 90% HNO_3 and the appropriate water washes were about 1.2 and 0.65% when the reaction temperatures were 25 and 93°C, respectively (Table 1). The loss was decreased to 0.15% with two 24-hr leaches with boiling acid (93°C). With specimens from sample 3H18, losses after two 4-hr leaches were about 0.1 and 0.03% when the leaching was conducted at 25 and 93°C, respectively (Table 1). In contrast to the results with 3% fuel, the loss was not decreased further by leaching the specimens twice for 24 hr with boiling 90% HNO_3 . The uranium recoveries from the irradiated specimens were essentially those expected from previous studies with similar unirradiated fuel specimens (5,8). Since the average uranium content of the KIWI-A core is about 10 wt %, an average recovery of >99% can be expected if the core is processed with boiling 90% HNO_3 .

Fission Product Behavior. The long-lived fission products Zr-95, Ru-106, Cs-137, and Ce-144 were leached from the graphite matrix more slowly than the uranium, at a different rate for each nuclide. For example, in two 4-hr leaches with boiling 90% HNO_3 the amounts of Zr-95, Ru-106, Cs-137, and Ce-144 leached were about 54, 66, 80, and 44%, respectively (Table 2). These data agree qualitatively with those reported elsewhere (9). Larger amounts of fission products were leached from specimens containing 12-15% uranium than from those

Table 1. Uranium Recovery by 90% HNO₃ from Irradiated KIWI-A Fuel Specimens

Burnup of specimens: ~0.001%

| Run No. | U in Sample, % | Leaching Conditions ^a | | Uranium Recovered, % | | | | |
|---------|----------------|----------------------------------|-----------------|----------------------|----------------------|-----------|----------------------|---------|
| | | Time, hr | Temp, °C | 1st Leach | 1st Leach and Washes | 2nd Leach | 2nd Leach and Washes | Residue |
| 4G1-1 | 3.00 | 4 | 25 | - | 95.4 | - | 3.5 | 1.1 |
| -3 | 2.81 | 4 | 25 | 60.1 | 95.1 | 2.6 | 3.6 | 1.3 |
| -2 | 3.02 | 4 | 93 ^b | 64.9 | 97.3 | 1.1 | 2.0 | 0.62 |
| -4 | 2.82 | 4 | 93 | 70.0 | 96.7 | 2.0 | 2.6 | 0.66 |
| -5 | 2.88 | 24 | 93 | 70.5 | 99.3 | 0.36 | 0.51 | 0.15 |
| 3H18-1 | 12.2 | 4 | 25 | - | 98.5 | - | 1.4 | 0.11 |
| -2 | 13.7 | 4 | 25 | 69.8 | 98.4 | 1.2 | 1.6 | 0.07 |
| -5 | 11.7 | 4 | 25 | 74.9 | 97.8 | 1.4 | 1.9 | 0.17 |
| -3 | 15.2 | 4 | 93 | 54.2 | 99.3 | 0.44 | 0.63 | 0.03 |
| -4 | 11.8 | 4 | 93 | 66.8 | 99.1 | 0.63 | 0.84 | 0.02 |
| -6 | 11.7 | 24 | 93 | 63.2 | 99.3 | 0.52 | 0.76 | 0.02 |
| -7 | 12.0 | 24 | 93 | 70.4 | 99.1 | 0.58 | 0.80 | 0.02 |

^aSpecimens subjected to two leaches, each for the time shown.

^bApproximate boiling point of 90% HNO₃.

containing ~3% uranium. The increase in fission product leaching was pronounced when the samples were leached twice for 24 hr instead of the usual 4 hr (Table 2, runs 3H18-6 and -7).

In several experiments to determine whether Ru-106 was volatilized from the boiling 90% HNO₃ solutions, as reported by Harwell workers (9) for dilute nitric acid solutions, there was no evidence of ruthenium volatilization.

Table 2. Fission Product Distribution in Two Leaches with 90% HNO₃ of Irradiated KIWI-A Fuel Samples

Burnup of specimens: ~0.001%

| Run No. | Amount of Nuclide in Sample, % | | | | | | | |
|---------|--------------------------------|-----------|----------------------|-----------|----------------------|-----------|----------------------|-----------|
| | Zr-95 | | Ru-106 | | Cs-137 | | Ce-144 | |
| | 1st Leach and Washes | Resi- due | 1st Leach and Washes | Resi- due | 1st Leach and Washes | Resi- due | 1st Leach and Washes | Resi- due |
| 4G1-1 | 41.6 | 38.2 | 39.6 | 46.3 | 17.2 | 80.7 | 20.8 | 75.7 |
| -3 | 12.4 | 81.9 | 40.1 | 41.2 | 88.6 | 8.11 | 23.5 | 69.1 |
| -2 | 49.2 | 40.0 | 55.1 | 36.0 | 60.3 | 31.4 | 19.7 | 62.1 |
| -4 | 37.8 | 54.2 | 51.2 | 43.6 | 69.0 | 22.4 | 21.0 | 55.3 |
| -5 | 67.9 | 20.5 | 51.9 | 22.7 | 85.4 | 13.0 | 66.8 | 26.8 |
| 3H18-1 | 8.2 | 46.2 | 24.5 | 63.2 | 58.6 | 28.0 | 23.1 | 74.4 |
| -2 | - | - | - | - | - | - | - | - |
| -5 | 14.7 | 79.6 | 26.5 | 57.5 | 47.5 | 38.0 | 20.6 | 75.9 |
| -3 | 26.7 | 59.5 | 49.3 | 36.7 | 69.5 | 21.1 | 30.7 | 61.3 |
| -4 | 61.4 | 29.7 | 65.2 | 19.2 | 82.3 | 7.12 | 37.4 | 43.6 |
| -6 | 45.0 | 33.8 | 54.9 | 27.3 | 81.7 | 6.9 | 47.5 | 17.9 |
| -7 | 44.8 | 31.8 | 58.4 | 22.2 | 79.9 | 8.51 | 52.2 | 26.6 |

Particle Size Data. The apparent geometric mean Stokes diameter of the powdered residues produced by the action of 90% HNO₃ on KIWI-A fuel specimens varied with the reaction temperature and time. In two 4-hr leaches, the mean diameter decreased from 300-400 to 200-300 μ when the reaction temperature was increased from 25°C to the boiling point (Table 3). In two 24-hr leaches with boiling acid, the mean diameter was decreased to 100-200 μ. More details of the effects of nitric acid concentration, uranium content of the fuel, and digestion time on particle size, are given in reference 5.

The apparent Stokes diameters of the particles were determined by a sedimentation method (10) assuming their densities to be 1.7 g/cc. The data were best correlated by log-probability plots (Fig. 1). The mean diameter obtained from such plots is the geometric mean (11,12); the geometric standard deviation, σ_g , is obtained from either

$$\log \sigma_g = \log (84\% \text{ size}) - \log (50\% \text{ size})$$

or

$$\log \sigma_g = \log (50\% \text{ size}) - \log (16\% \text{ size}).$$

Table 3. Size of Particles in Residue from 90% HNO₃ Leaching of Irradiated KIWI-A Fuel Specimens

Each specimen leached twice for time indicated

| U in Sample, % | Leaching Conditions | | Geom. Mean Stokes Dia, μ | Geom. Stand. Deviation |
|----------------|---------------------|--------------------------|------------------------------|------------------------|
| | Time, hr | Temp, $^{\circ}\text{C}$ | | |
| 2.81 | 4 | 25 | 295 | 1.83 |
| 11.7 | 4 | 25 | 390 | 2.11 |
| 12.2 | 4 | 25 | 390 | 2.11 |
| 2.82 | 4 | 93 | 208 | 1.71 |
| 3.02 | 4 | 93 | 295 | 1.74 |
| 11.8 | 4 | 93 | 213 | 1.90 |
| 15.2 | 4 | 93 | 259 | 1.99 |
| 2.88 | 24 | 93 | 112 | 1.24 |
| 11.7 | 24 | 93 | 149 | 1.62 |
| 12.0 | 24 | 93 | 187 | 1.62 |

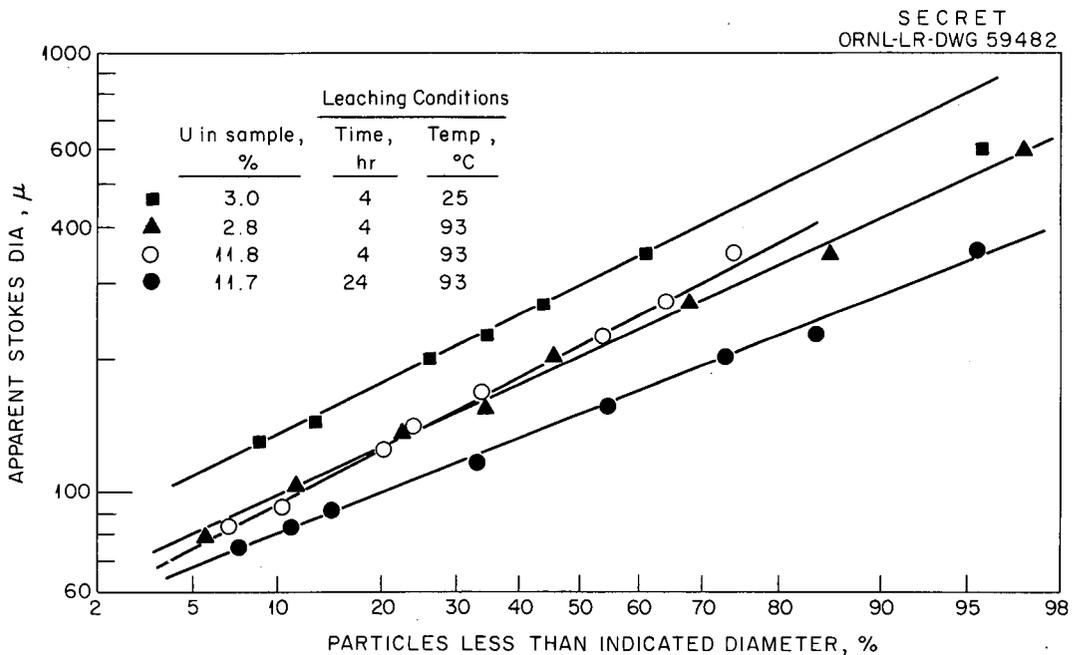


Fig. 1. Log-probability plots of particle size data obtained in 90% HNO₃ disintegration of KIWI-A fuel specimens. Each specimen leached twice for the indicated time.

2.3 NbC-coated KIWI-A', -A3, and -B Fuels

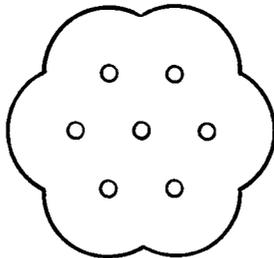
Leaching of specimens of these fuels with boiling 90% HNO₃ under flow-sheet conditions (8) (see Sect. 2.1) resulted in uranium losses of 0.8 to 7%, depending on the niobium content of the fuel (Table 4 and Fig. 2). The losses increased almost exponentially from about 0.03 (KIWI-A) to about 7% as the niobium content increased from 0 to about 14% (Fig. 2). Leaching

Table 4. Recovery of Uranium from KIWI Fuel Specimens by the 90% HNO₃ Process

| Fuel Type | Comp, % | | Temp, °C | Uranium Recovery, % | | | | Residue |
|-----------|---------|------|----------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|---------|
| | U | Nb | | 1st Leach ^a and Washes | 2nd Leach ^a and Washes | 3rd Leach ^a and Washes | 4th Leach ^a and Washes | |
| A' | 4.73 | 5.28 | 93 | 96.8 | 2.13 | 0.18 | - | 0.79 |
| A' | 4.68 | 5.97 | 93 | 97.6 | 1.18 | - | - | 1.22 |
| A' | 4.65 | 5.28 | 93 | 96.7 | 2.26 | 0.12 | 0.07 | 0.89 |
| A3 | 4.57 | 6.05 | 93 | 95.6 | 1.87 | - | - | 2.53 |
| B | 16.7 | 11.5 | 25 | 91.9 | 2.64 | - | - | 5.47 |
| B | 17.0 | 11.2 | 93 | 94.0 | 1.43 | - | - | 4.54 |
| B | 16.5 | 13.0 | 93 | 94.7 | 0.84 | 0.08 | - | 4.38 |
| B | 16.6 | 12.6 | 93 | 91.6 | 0.99 | 0.16 | - | 7.24 |
| B | 16.4 | 10.0 | 93 | 94.7 | 1.46 | 0.22 | - | 3.60 |

^aEach leach, 4 hr.

the fuels three or four times instead of twice increased the recovery only 0.2% (Table 4). The experiments were conducted with unirradiated KIWI-A' and -A3 specimens supplied by LASL and with KIWI-B specimens fabricated at Y-12. The KIWI-B specimens were of the 7-hole variety:



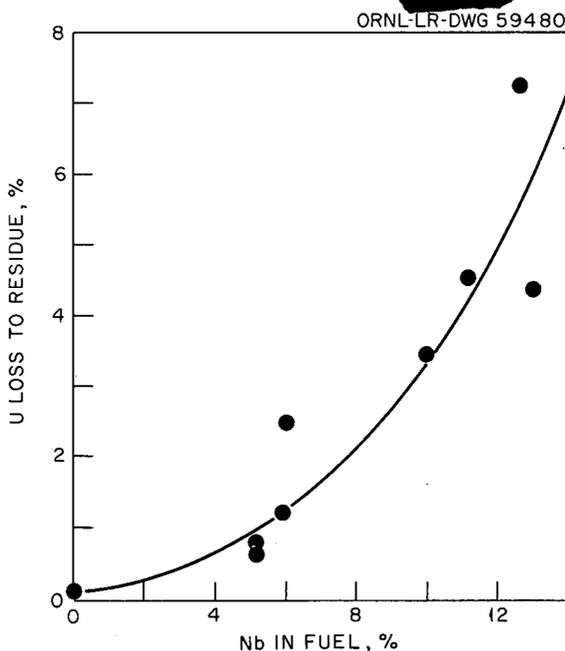


Fig. 2. Effect of niobium content on uranium losses to residues in two 4-hr leaches of KIWI fuel specimens with boiling 90% HNO_3 .

High uranium losses were not unexpected since the NbC coatings, which were unaffected by concentrated nitric acid (cf. Sect. 5.0), contained some dissolved uranium carbide (3,13). Chemical analysis of a coating from a KIWI-B sample showed it to contain 2.4% uranium, a concentration too low to be detected by x-ray analysis. This observation accounts for the fact that only NbC was identified by x-ray analysis of pieces of coating remaining after three leaches with boiling 90% HNO_3 .

A modified 90% HNO_3 process, in which the NbC coating was dissolved in HNO_3 -HF solution, resulted in almost complete uranium recovery from a KIWI-A3 fuel specimen. The fuel specimen containing 4.62% uranium and 5.8% niobium was disintegrated and leached with boiling 90% HNO_3 for 4 hr; then about two-thirds of the leach solution was removed by decantation. Enough 10 N HF was added to the moist residue at room temperature to produce a solution about 10 M HNO_3 -5 M HF. The residue was soaked in this solution at room temperature for 1 hr and then the solution was removed by vacuum filtration. After the residue had been thoroughly washed with water it was leached again for 4 hr with boiling 90% HNO_3 . This treatment completely dissolved the NbC coatings and recovered 99.9% of the uranium:

| Solution | Amount Recovered, % | |
|--|---------------------|---------|
| | Uranium | Niobium |
| First 90% HNO ₃ leach | 56.9 | 0 |
| 10 M HNO ₃ —5 M HF soak | 19.4 | 67.8 |
| Water washes | 14.6 | 32.2 |
| Second 90% HNO ₃ leach and washes | 8.9 | - |
| Residue | 0.09 | <0.01 |

The conditions of this experiment were not necessarily optimum. Other experiments are required to define the minimum concentration of fluoride ion required to minimize container corrosion. The experiment did show, however, that uranium can be recovered from NbC-coated KIWI fuel elements if the NbC is completely dissolved.

Log-probability plots of sieve fractions of the residues from 90% HNO₃ leaching of NbC-coated fuel specimens showed two distinct linear regions (Fig. 3). Visual inspection of these fractions showed that most of the material that was larger than 60 mesh (the approximate intersection point of the two linear regions) was NbC. Chemical analyses confirmed this observation:

| Run No. | Amount of NbC, % | |
|---------|---------------------|----------------------|
| | Larger than 60 mesh | Smaller than 60 mesh |
| 1 | 90.9 | 9.1 |
| 2 | 98.7 | 1.3 |
| 3 | 84.3 | 15.7 |

Each sieve fraction from an experiment with KIWI-B material was chemically analyzed. The amount of uranium retained in each fraction was proportional to the amount of niobium in that fraction (Table 5). About 50 wt % of the residue was larger than 60 mesh; this portion contained about 99 and 3.3% of the niobium and uranium, respectively, present in the original specimens. The other half of the residue, which was finer than 60 mesh, contained only 0.3% of the total uranium. These data strongly suggest that NbC-UC solid solutions of low UC content are as unreactive to nitric acid as pure NbC.

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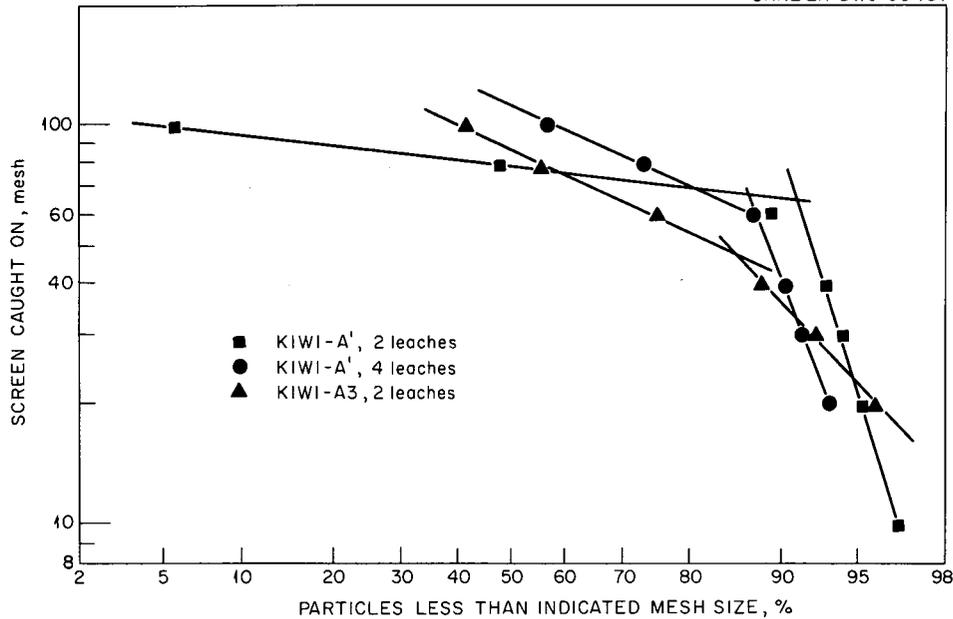


Fig. 3. Log-probability plots of particle size data obtained by sieving residues from 90% HNO₃ disintegrations of NbC-coated KIWI fuel specimens. Each leach, 4 hr with boiling acid.

Table 5. Amounts of Niobium and Uranium in Sieve Fractions of Powdered Residue from 90% HNO₃ Disintegration of KIWI-B Fuel

| Residue Sieve Caught on, mesh | Amount, % of total | Amount of Residue, % of total in orig. spec. ^a | |
|-------------------------------------|-----------------------|--|---------|
| | | Niobium | Uranium |
| 10 | 6.8 | 30.6 | 0.6 |
| 20 | 17.6 | 49.1 | 1.4 |
| 30 | 6.8 | 14.5 | 0.6 |
| 40 | 4.5 | 3.6 | 0.4 |
| 60 | 12.5 | 1.3 | 0.2 |
| 80 | 20.8 | 0.3 | 0.1 |
| 100 | 4.1 | 0.2 | 0.04 |
| pan | 27.0 | 0.3 | 0.2 |

^aOriginal specimen contained 3.03 g of Nb and 4.86 g of U.

~~3.0~~ 3.0 COMBUSTION-DISSOLUTION PROCESS

3.1 Flowsheet

Definite flowsheet conditions have not been developed. The sequence of steps, however, will probably be: (a) crushing of the fuel elements; (b) charging of the fuel to a burner; (c) combustion of the fuel in oxygen at temperatures $>800^{\circ}\text{C}$; (d) dissolution of the oxide ash in a nitric acid solution; and (3) adjustment of the acidic solution for solvent extraction. The composition of the dissolvent will be dictated by the type and amounts of impurities in the fuel. For example, the presence of iron in the KIWI-A fuel makes it mandatory that HCl be present in the dissolvent if the combustion ash is to be completely dissolved.

3.2 KIWI-A Fuel

Effect of Iron Impurity on Uranium Recovery. The KIWI-A fuel specimens contained between 0.1 and 0.3% iron as an impurity:

| <u>Fuel Plate</u> | <u>U, %</u> | <u>Fe, %</u> | <u>Fuel Plate</u> | <u>U, %</u> | <u>Fe, %</u> |
|-------------------|-------------|--------------|-------------------|-------------|--------------|
| 4G1 | 2.98 | 0.11 | 3H18 | 10.9 | 0.32 |
| | 3.04 | 0.11 | | 11.8 | 0.32 |
| | 2.88 | 0.11 | | 11.4 | 0.32 |

The source of the impurity was not definitely established, but is believed to be the graphite fixtures (or "cassettes") that hold the elements during baking and graphitization (13). It could also have been introduced as an impurity in the graphite flour from which the elements were molded (14).

On combustion of KIWI-A fuel samples, the iron was converted to iron oxide which could not be dissolved in boiling 8-10 M HNO_3 in 24 hr. However, combustion residues were completely dissolved in less than 4 hr in boiling 8 M HNO_3 -0.75 M HCl. In some cases, a small amount of residue remaining after dissolution of the combustion ash in HNO_3 -HCl solution was shown by x-ray analysis to be SiO_2 . Dissolution of the iron oxide was not complete in 4 hr when the HCl concentration was less than 0.75 M. Complete dissolution of the ash appears essential to avoid loss of uranium to the nitric acid-insoluble iron-bearing component. Uranium losses as a function of iron content of the fuel have not yet been determined. However, with a specimen of plate

4G1 containing 0.1% iron, the loss to the iron-bearing residue was 0.2% after 6 hr digestion of the combustion ash in boiling 10 M HNO₃.

Fission Product Behavior. When KIWI-A fuel specimens were burned in a flowing stream of oxygen at 900°C, a significant portion of the Ru-106 was volatilized. With fuel specimens from plate 4G1 (containing about 3% uranium), 60-95% of the ruthenium volatilized; from specimens of plate 3H18, containing about 11% uranium, only about 40% of the ruthenium volatilized (Table 6). No explanation for this behavior can be offered at this time. Neither uranium, Zr-95, Cs-137, nor Ce-144 was volatilized during combustion.

Table 6. Distribution of Ru-106 in Combustion of KIWI-A Fuel Element Specimens

Burnup of specimens: ~0.001%

| Exp. No. | U in Sample, % | Amount of Ruthenium in Indicated Sample, % | | | | | | Total Volatilized |
|----------|----------------|--|------------------|--------------|--------------|--------------|--------------|-------------------|
| | | Comb. Ash | Cool End of Tube | 1st Scrubber | 2nd Scrubber | 3rd Scrubber | 4th Scrubber | |
| 1 | 2.98 | 40.1 | 59.8 | 0.1 | 0.06 | - | - | 59.9 |
| 2 | 3.04 | 5.7 | 94.0 | 0.2 | 0.07 | 0.02 | 0.005 | 94.3 |
| 3 | 2.88 | 8.5 | 91.3 | 0.08 | 0.06 | 0.02 | 0.01 | 91.5 |
| 4 | 10.9 | 62.0 | 37.8 | 0.1 | 0.03 | 0.007 | - | 38.0 |
| 5 | 11.8 | 53.2 | 46.5 | 0.1 | 0.1 | 0.02 | 0.009 | 46.8 |
| 6 | 11.4 | 59.6 | 40.4 | 0.04 | 0.02 | 0.006 | - | 40.4 |

The specimens, contained in porcelain boats, were burned in a furnace-heated 1-in.-dia quartz tube connected to four scrubbers, in series, containing 5 N NaOH. The distance from the combustion boat to the cool (100°C) exit end of the tube was about 10 in.; the temperature drop across this distance was at least 800°C. A Ca(OH)₂ bubbler at the end of the train showed that no CO₂ passed through the scrubbers. To determine the total amount of ruthenium distributed throughout the system six samples were analyzed, one from the dissolution of the combustion ash, one from the leaching of the exit end of the reaction tube, and one from each of the four scrubbers. Any ruthenium not found with the combustion ash was considered to have been volatilized.

3.3 KIWI-A', -A3, and -B Fuels

Only preliminary combustion experiments have been performed with un-irradiated specimens of these fuels. The results, while not conclusive, indicate that uranium cannot be completely leached from the $U_3O_8-Nb_2O_5$ combustion ash with boiling 10 M HNO_3 . Losses to the acid-insoluble residue were as high as 2.9%:

| <u>Fuel Type</u> | <u>Composition, %</u> | | | <u>U Loss to Residue,^a %</u> |
|------------------|-----------------------|-----------|-----------|---|
| | <u>U</u> | <u>Nb</u> | <u>Fe</u> | |
| A' | 7.67 | 2.27 | - | 0.24 |
| A3 | 4.51 | 4.90 | 0.03 | 2.88 |
| B | 16.3 | 10.1 | 0.01 | 0.03 |

^aCombustion ash leached 4 hr with boiling 10 M HNO_3 .

Both Fe_2O_3 and Nb_2O_5 are present in the combustion ash and are not dissolved in nitric acid. The relative effects on the uranium loss of these constituents has not yet been established, although the data given in the above tabulation show that the residue is chiefly Nb_2O_5 . This is unfortunate, since Nb_2O_5 is insoluble in nearly all aqueous reagents.

4.0 GRIND-LEACH PROCESS

4.1 Flowsheet

A tentative reference flowsheet has been reported (6,7). Fuel elements are first ground fine enough to pass a 16 mesh screen and then leached with boiling 70% (15.8 M) HNO_3 for 4 hr. For this first leach, 5 liters of acid per kilogram of fuel is used. After water-washing, the fuel is leached again for 4 hr with boiling 15.8 M HNO_3 (2.5 liters per kilogram of fuel). A final water-wash removes traces of sorbed uranium-bearing solution.

4.2 Experiments with KIWI Fuels

Samples of unirradiated KIWI-A, -A', and -B fuels were leached twice with boiling 15.8 M HNO_3 under flowsheet conditions (6,7). As in the 90% HNO_3 experiments (Sect. 2.3), the uranium losses to the graphite residues were

proportional to the amounts of niobium in the fuel. For example, with specimens ground to pass a 200 mesh screen, the uranium loss to the residue increased from 0.09 to 3.3% when the niobium content of the fuel increased from 0 to 8% (Table 7). Although recoveries from the A' and B specimens were higher than those obtained with the 90% HNO₃ treatment, they were still considerably lower than desired. Furthermore, since grinding should have little effect on the reactivity of NbC-UC solid solutions in nitric acid, complete uranium recovery is again dependent on dissolution of the NbC.

Table 7. Recovery of Uranium from KIWI Fuel Element Specimens by the Grind-Leach Process

| Fuel Type | Comp, % | | Mesh Size ^a | Uranium Recoveries, ^b % | | | | |
|-----------|---------|------|------------------------|------------------------------------|--------|-----------|--------|---------|
| | U | Nb | | 1st Leach | Washes | 2nd Leach | Washes | Residue |
| A | 4.56 | 0 | 16 | 90.1 | 9.19 | 0.20 | 0.13 | 0.34 |
| A | 3.47 | 0 | 200 | 92.1 | 7.48 | 0.23 | 0.05 | 0.09 |
| A' | 8.84 | 2.87 | 16 | 88.5 | 10.2 | 0.22 | 0.04 | 1.08 |
| A' | 7.65 | 2.36 | 200 | 85.1 | 13.3 | 0.23 | 0.03 | 1.28 |
| B | 16.4 | 12.5 | 16 | 87.6 | 8.71 | 0.12 | 0.02 | 3.53 |
| B | 16.4 | 8.0 | 200 | 87.7 | 8.75 | 0.24 | 0.04 | 3.32 |

^aSamples ground to pass the indicated screen size.

^bSamples leached twice for 4 hr with boiling 70% HNO₃.

5.0 DISSOLUTION OF NIOBIUM CARBIDE

Studies of the dissolution of NbC in aqueous reagents were started in the hope of evolving a satisfactory method for dissolving the KIWI fuel element coatings. Niobium carbide did not dissolve in either boiling HNO₃ or HF solutions but dissolved in mixtures of these acids. In solutions where the HNO₃ concentration was less than 16 M, the initial rate of dissolution increased with both increasing HF and HNO₃ concentrations and was maximum when the HNO₃ concentration was 12-16 M. Other reagents, NH₄F, NaOH, HNO₃-HCl, and H₂SO₄, did not effect any significant dissolution.

Results reported elsewhere (15) show that NbC is soluble only in HF-HNO₃ solution, in which its behavior is similar to that of niobium metal (16) but quite different from that of zirconium metal (17) whose dissolution is little affected by changes in the nitric acid concentration. Although the stoichiometry has not yet been determined, acid consumption can be estimated by assuming the reaction



5.1 Dissolution Tests

Of all the reagents tested, NbC dissolved only in HF-HNO₃ solutions; it was virtually unaffected by either component alone:

| Conc, M | | Time, hr | Amount of NbC Dissolved, % |
|------------------|-----------------|-------------|-------------------------------|
| HNO ₃ | HF | | |
| 10 ^a | 0 | 9.1 | 0 |
| 0 | 1 | 0.7 | 0.04 |
| 0 | 4 | 8.9 | 0.11 |
| 0 | 6 | 9.4 | 0.04 |
| 0 | 10 ^a | 9.7 | 0.18 |

^aFilm formed on specimen.

Initial dissolution rates in HNO₃-HF were markedly affected by changes in both the nitric and hydrofluoric acid concentrations. With a constant HF concentration, rates were maximum when the HNO₃ concentration was 12-16 M (Table 8, Fig. 4). When the HNO₃ concentration was constant but less than 16 M, the rates increased with increasing HF concentration; for example, in 5 M HNO₃, the rate increased from essentially 0 to about 7.2% per minute when the HF concentration increased from 0 to 5 M. The decrease in initial rate in solutions with HNO₃ concentrations >16 M was due to the formation of an unidentified passive film on the surface of the specimens. The chief effect of increasing the HF concentration in the concentrated HNO₃ solutions was dissolution of a larger portion of the specimen before passivation was complete:

| Dissolvent | Amount Dissolved, % | Approx. Time Required for Complete Passivation of Specimen, hr |
|-----------------------------------|---------------------------|---|
| 19.7 M HNO ₃ —0.5 M HF | 1.46 | 1.6 |
| 19.7 M HNO ₃ —1.0 M HF | 9.56 | 5.4 |
| 19.7 M HNO ₃ —2.0 M HF | 13.3 | 5.4 |

Table 8. Initial Rates of Dissolution of NbC
in Boiling HF-HNO₃ Solutions

Conditions: 0.5- to 1-g specimen; 150 ml of dissolvent

| Conc, M | | Amount of Specimen Dissolved, % | Initial Rate, %/min |
|------------------|------|------------------------------------|------------------------|
| HNO ₃ | HF | | |
| 1.0 | 0.1 | 0.06 | 0.0002 |
| | 0.5 | 0.07 | 0.0003 |
| | 1.0 | 0.24 | 0.0008 |
| | 3.0 | 4.5 | 0.064 |
| | 5.0 | 3.56 | 0.15 |
| | 7.0 | 3.67 | 0.46 |
| | 10.0 | 5.5 | 2.0 |
| 2.0 | 0.1 | 9.82 | 0.18 |
| | 0.5 | 4.51 | 0.30 |
| | 1.0 | 4.83 | 0.37 |
| | 3.0 | 6.15 | 1.5 |
| | 5.0 | 3.04 | 2.0 |
| | 7.0 | 3.87 | 2.9 |
| | 10.0 | 7.69 | 6.9 |
| 5.0 | 0.1 | 5.08 | 0.22 |
| | 0.5 | 5.62 | 1.5 |
| | 1.0 | 3.16 | 2.9 |
| | 3.0 | 5.05 | 5.5 |
| | 5.0 | 4.82 | 7.2 |
| 10.0 | 0.1 | 0.40 | 0.36 |
| | 1.0 | 2.94 | 4.1 |
| | 3.0 | 4.81 | 8.2 |
| 14.8 | 0.5 | 1.59 | 0.96 |
| | 1.0 | 3.98 | 4.5 |
| | 2.0 | 3.51 | 4.4 |
| | 3.0 | 7.5 | 9.0 |
| 19.7 | 0.5 | 0.89 | 0.40 |
| | 1.0 | 2.04 | 0.98 |
| | 2.0 | 1.19 | 1.1 |

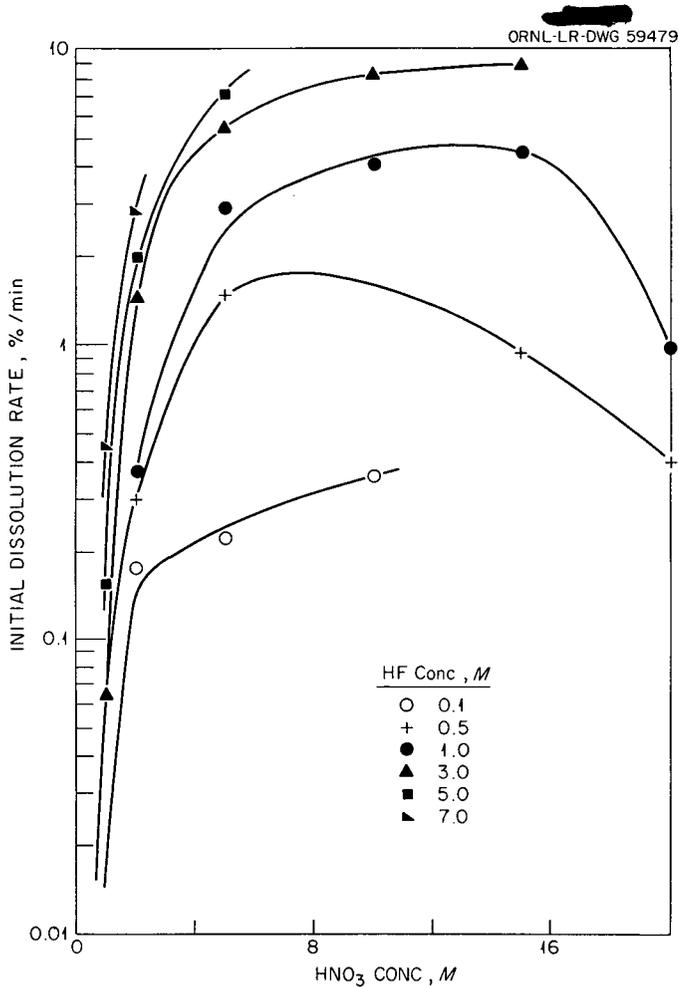


Fig. 4. Initial rates of dissolution of NbC in boiling HF-HNO₃ solutions; less than 10% of specimen dissolved in each case.

The terminal Nb concentration in the series with 19.7 M HNO₃ was always less than 0.8 g per liter. In the 14.8 M HNO₃ series, partial film formation was noted almost immediately in solutions containing 0.5-3 M HF. No films were formed at lower HNO₃ concentrations. The film may have been Nb₂O₅ or NbO₂F, which apparently is quite insoluble in solutions of high HNO₃ concentration.

Dissolution was complete in about 2 hr in boiling 2-6 M HNO₃ containing 3-6 M HF. However, in several of the solutions, a precipitate formed after cooling, which was tentatively identified as NbO₂F by x-ray and chemical analyses. Data from the complete dissolution experiments indicated that the solubility of NbO₂F was <20 g of Nb per liter in solutions containing

2-6 M HNO_3 and probably less than 1 g of Nb per liter when the HNO_3 concentration was 15-20 M. The NbO_2F was insoluble in water and acetone.

The above data suggest that dissolution of NbC might be best carried out in 2-5 M HNO_3 containing 0.1-0.5 M HF where the niobium solubility is relatively high and corrosion of the dissolver vessel may not be too severe.

Attempts to dissolve NbC in boiling 1-16 M NaOH, 6 M NH_4F to which 30% H_2O_2 was continuously added, 5 M HNO_3 —2 M HCl, 2 M HNO_3 —4 M HCl, 4-6 M H_2SO_4 , 10 M HCl, and 6 M H_3PO_4 all were unsuccessful. In each case the NbC specimens showed little or no weight loss in digestion periods up to 10 hr.

5.2 Procedure

In each experiment, less than 10% of the specimen was dissolved; therefore the rate obtained was considered a close approximation to the initial rate. The rates were expressed in %/min because of the irregular shape of the specimens, which were obtained by fracturing 20-g buttons produced by an arc-melting procedure. Each specimen (0.5-1 g) was digested with 150 ml of boiling dissolvent, and the contents of the dissolver were quickly poured into a large volume of cold water. The solid remains of the specimen were removed, washed with acetone, dried, and weighed to determine the extent of dissolution.

The apparatus used for determining rates in the fluoride-bearing solutions was a 225-ml Teflon vessel and a Teflon condenser connected by a two-neck standard-taper glass adapter. With solutions of high HF concentration, attack of the glass portion of the apparatus was particularly severe, and Na_2SiF_6 was frequently found as a solid residue after a dissolution.

5.3 Preparation and Purity of Specimens

Two types of NbC buttons were prepared* by an arc-melting technique, one from high-purity niobium powder and the other from niobium foil. Complete dissolution of specimens of each type in boiling 6 M HNO_3 —6 M HF indicated no unreacted carbon in the specimens made from niobium powder and only traces (<0.1%) in a few of the samples made from foil. Chemical analyses indicated that the specimens contained 10-20 mol % free niobium (Table 9). X-ray analyses showed only the presence of NbC in the specimens; trace amounts of copper, iron, molybdenum, silicon (all 0.01-0.1%), magnesium (0.0001-0.001%), and tungsten (0.1-1%) were detected by spectroscopic analysis.

* D. T. Bourgette, ORNL Metallurgy Division.

Table 9. Analysis of NbC Specimens Used in Dissolution Studies

| Specimen Made from | Amount of Free Carbon, % | Chemical Analysis, ^a wt % | | Nb/C Mole Ratio |
|-----------------------|-----------------------------|---|--------|--------------------|
| | | Niobium | Carbon | |
| Powder | - | 89.5 | 10.5 | 1.10 |
| Powder | 0 | 87.9 | - | - |
| Powder | 0 | 86.8 | - | - |
| Powder | - | 89.7 | - | - |
| Powder | - | 88.7 | 9.60 | 1.19 |
| Foil | 0.1 | 89.7 | 9.52 | 1.22 |
| Foil | 0 | - | - | - |

^aCalculated for NbC: Nb, 88.5%; C, 11.5%.

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