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# AQUEOUS PROCESSES FOR URANIUM RECOVERY FROM ROVER FUEL ELEMENTS: LABORATORY DEVELOPMENT

## PART III. SUMMARY OF THE PROCESSES

(Title Unclassified)

L. M. Ferris
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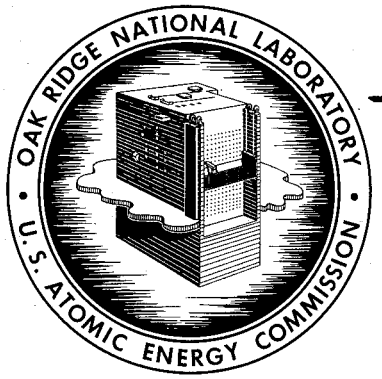




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# AQUEOUS PROCESSES FOR URANIUM RECOVERY FROM ROVER FUEL ELEMENTS: LABORATORY DEVELOPMENT. PART III. SUMMARY OF THE PROCESSES


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# AQUEOUS PROCESSES FOR URANIUM RECOVERY FROM ROVER FUEL ELEMENTS: LABORATORY DEVELOPMENT. PART III. SUMMARY OF THE PROCESSES

L. M. Ferris
K. S. Warren

## ABSTRACT

The development of aqueous methods for processing Rover fuel elements is summarized. The Rover fuel elements are dispersions of carbon-coated $UC_2$ particles in graphite matrices; hydrogen coolant channels in the elements are lined with NbC to retard corrosion. Since the coated particles are impervious to attack by aqueous reagents, burning of the fuel is necessary at one stage of the process.

The two main processes under development are (1) the Deline-Burn-Dissolve (DBD) process, and (2) the Burn-Dissolve process. Both processes result in almost quantitative uranium recovery; however, based on the laboratory experiments, the DBD process appears to have the best chance of success on an engineering scale.

The DBD process involves dissolution of the NbC liners in 10 M $HNO_3$--3 M HF (F/Nb mole ratio of 8) in plastic equipment, washing of the delined fuel with water to remove the residual fluoride-bearing solution, transferring the fuel to a burner (Corronel 230 appears to be the best material of construction), burning in oxygen at 800 to 1000°C, and dissolution of the $U_3O_8$ ash in 6 M $HNO_3$. The aqueous solutions are combined to produce a solution containing about 1 M HF, 4 M $HNO_3$, 0.125 M niobium, and 0.07 M uranium, from which the uranium can be recovered by extraction with tributyl phosphate or dibutyl-butyl phosphonate. In an alternative procedure, the small amount of uranium present in the delining solution can be removed by extraction and the fluoride-bearing raffinate discharged to waste. Most of the uranium from the fuel is therefore decontaminated and recovered from the highly concentrated (300 g/liter) solution obtained by dissolution of the combustion ash in nitric acid.

In the Burn-Dissolve process, the fuel elements are burned directly in oxygen at 800 to 1000°C, the $U_3O_8$-$Nb_2O_5$ ash transferred to a plastic dissolver, and the ash dissolved in 4 M $HNO_3$--1 M HF (F/Nb mole ratio of at least 60) to provide the feed for solvent extraction.

Studies in support of process development were conducted: investigation of the factors affecting delining and ash dissolution, measurement of the solubility of niobium in HF-$HNO_3$ solutions, and corrosion testing of several potential materials of construction.

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## 1. INTRODUCTION

The purpose of this report is to summarize the laboratory development of aqueous processes for recovering uranium from Rover reactor fuels. The work reported here was conducted at ORNL during the period July 1, 1962 to April 1, 1963. The Rover nuclear rocket reactors will contain fuel elements consisting of carbon-coated uranium carbide particles dispersed throughout a graphite matrix.[1] Channels (holes) in the elements, which allow passage of the hydrogen propellant, are partially lined with NbC.

The processing of Rover and other graphite-base reactor fuels has been studied at ORNL since 1957.[2-8] The first Rover fuels were dispersions of uncoated uranium oxide or carbide particles in a graphite matrix. Several potential processing methods, including the 90%-$HNO_3$ disintegration-leach process[7] and the Grind-Leach process,[8] were developed for this type of fuel.[5-8] However, the decision to use coated (or "beaded") particles in the Rover fuel elements necessitated a marked change in aqueous processing policy. This fuel change probably eliminated the 90%-$HNO_3$ process from consideration, put severe restrictions on the Grind-Leach process, and necessitated the development of newer processes to cope with the problem of the coated particles. A Combustion--Fluoride Volatility procedure has received major emphasis at ORNL;[9] this effort is supplemented by the development of alternative Aqueous and Chloride Volatility processes.[10,11]

Aqueous processes being developed for the coated particle Rover fuels are basically Deline-Burn-Dissolve (DBD) and Burn-Dissolve methods. Work on these, and other potential alternatives, is summarized here. This report contains tentative flowsheets for both the DBD and Burn-Dissolve processes, results of investigations of the factors affecting dissolution of NbC and $Nb_2O_5$ in $HNO_3$-HF solutions,

and other chemical data obtained in the course of process development. Since very little coated-particle Rover fuel was available for these studies, samples of Kiwi-BIA fuel were used. This fuel (7-hole) was lined with NbC, but the uranium carbide fuel particles were not carbon coated. Burning of Rover fuels is now being studied on an engineering scale; the results of that study will be reported elsewhere, as will those obtained in the development of both the Fluoride and Chloride Volatility processes.

The authors wish to thank A. H. Kibbey for her aid in conducting the electrolytic disintegration experiments and designing the Teflon dissolving apparatus. Analyses were provided by the ORNL Analytical Chemistry Division, in particular, the groups of W. R. Laing, H. Dunn, and R. L. Sherman.

## 2. DEVELOPMENT OF THE DELINE-BURN-DISSOLVE PROCESS

The DBD process basically involves the following sequence of operations: (1) dissolving the NbC liners in $HF-HNO_3$ solution; (2) washing the delined fuel with water to remove residual fluoride-bearing solution; (3) burning the delined and washed fuel in oxygen to convert the graphite to gaseous $CO_2$ and the uranium to $U_3O_8$; (4) dissolution of the $U_3O_8$ in nitric acid. In one variation of the DBD process, all the aqueous solutions are combined to produce a fluoride-containing solvent extraction feed solution of low uranium concentration. An alternative scheme involves extraction of the uranium directly from the combined delining and wash solutions; the raffinate is discharged to waste, thus eliminating fluoride from other parts of the system. The uranium is recovered from the organic extract by stripping with acid; the $U_3O_8$ ash is dissolved in nitric acid (producing a high-uranium-concentration solution)and the uranium recovered by solvent extraction. The major objectives of these methods are to provide for maximum uranium recovery, to minimize the amount of hydrofluoric acid used, and to produce solutions from which the uranium can be readily decontaminated and recovered by conventional solvent extraction techniques.

### 2.1 Tentative Deline-Burn-Dissolve Flowsheets

The tentative flowsheets (Figs. 1a and 1b) are based on the experimental data given in Sec. 2.3 and the basic assumption that the coatings from some of the fuel

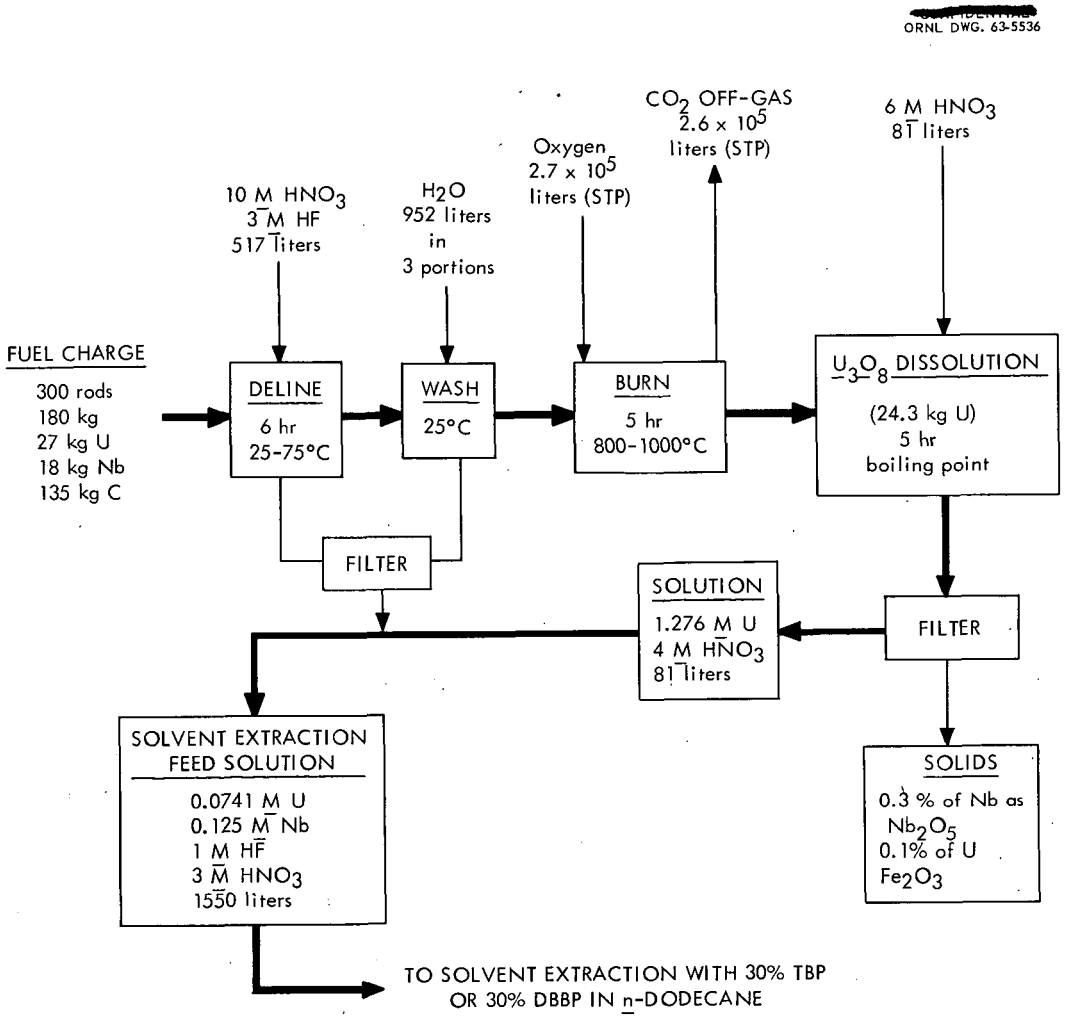


Fig. 1a. Tentative Deline-Burn-Dissolve Flowsheet for Processing Coated-Particle Rover Fuels in Which All the Aqueous Solutions are Combined Prior to Solvent Extraction.

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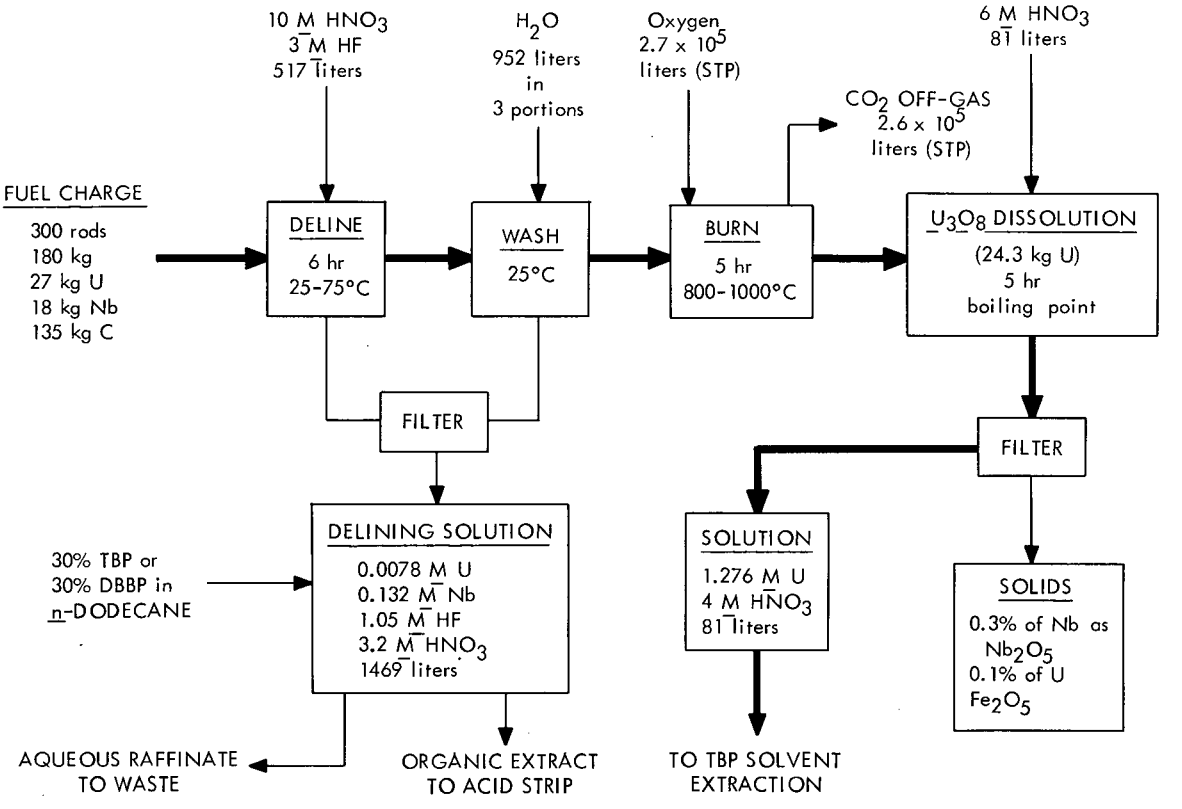


Fig. 1b. Tentative Deline-Burn-Dissolve Flowsheet for Processing Coated-Particle Rover Fuels in Which Uranium is Extracted from Delining Solution and Most of Uranium in the Fuel is Recovered from $HNO_3$ Solutions Containing 300 g of Uranium per liter.

particles will be destroyed during reactor operation and that, therefore, some uranium will migrate from the exposed particles into the NbC liner and will be dissolved during the delining step. Other conditions used in calculating the volumes, etc., given in the flowsheets are:

1. Fuel composition: 75% C; 15% U; and 10% Nb.
2. F/Nb mole ratio* for delining: 8.
3. Amount of uranium dissolved during delining: 10%.
4. Stoichiometric consumption of oxygen during the burning operation:

   $C + O_2 \longrightarrow CO_2$; $3UC_2 + 10\ O_2 \longrightarrow U_3O_8 + 6CO_2$;

   $4NbC + 9\ O_2 \longrightarrow 2Nb_2O_5 + 4CO_2$.
5. HF concentration in the combined solvent extraction feed solution: 1 M.

Under the tentative flowsheet conditions, the fuel elements (either intact or crushed) are digested with 10 M $HNO_3$--3 M HF (F/Nb mole ratio of 8) for 6 hr. Because $HNO_3$-HF solutions are extremely corrosive to metallic vessels, the delining vessel will probably have to be constructed of plastic. The reaction is initiated at room temperature, but, since the delining reaction is highly exothermic (a rise in temperature to about 70°C is common in laboratory experiments), the plastic vessel should not require external heating. During the 6-hr delining period, about 99.7% of the niobium is dissolved (see Sec. 2.2). After the delining solution is removed by filtration, the fuel is washed three times with water to reduce the fluoride content of the fuel to less than 0.3%. Minimization of the fluoride content by washing is important if excessive corrosion during the subsequent burning operation is to be avoided.

The delined and washed fuel is then burned in oxygen at 800 to 1000°C, probably in a Corronel 230 burner. Corronel 230, or a stainless steel, is preferred for the burner so that combustion and dissolution of the $U_3O_8$ ash can be achieved in the same vessel. In this way, transfer of the solid ash to a separate dissolver can be avoided.

*Throughout this report, F/Nb mole ratio refers to the total number of moles of fluoride in the system divided by the total number of moles of niobium in the fuel sample.

With delined and washed fuel containing less than 0.5% fluoride, burning at temperatures below 1000°C should result in corrosion rates of less than 0.1 mil/month over the combustion-dissolution cycle (see Sec. 2.5). The $U_3O_8$ combustion ash dissolves in less than 5 hr in boiling 6 M $HNO_3$, yielding a solution containing 300 g of uranium per liter. This solution is filtered to remove the small amounts of insoluble $Nb_2O_5$ (containing about 0.3% of the original niobium) and iron oxide present in the ash. These insolubles retain less than 0.1% of the total uranium.

The delining solution, the wash solutions, and the solution obtained from dissolution of the combustion ash can be combined to produce a stable solvent extraction feed solution containing 0.074 M uranium, 0.125 M niobium, 1 M HF, and about 3 M $HNO_3$ (Fig. 1a). Uranium can be extracted from this feed solution with 30% solutions of either tributyl phosphate (TBP) or dibutyl-butyl phosphonate (DBBP) in n-dodecane. The distribution coefficient with TBP is about 1, while the DBBP gives a coefficient of about 10.[12] Extraction of the uranium from the fluoride-containing solution can possibly be conducted in stainless steel equipment at room temperature (Sec. 2.5). If corrosion of metals is too severe, plastic or plastic-lined solvent extraction equipment will be required.

The alternative DBD process (Fig. 1b) is designed specifically to avoid the presence of fluoride in the main solvent extraction system. After the delining and wash solutions are combined in a plastic vessel, the small amount of uranium present can be removed by extraction with either TBP or DBBP. Most of the fluoride remains with the aqueous raffinate, which is discharged to waste. The organic extract can then be blended into the stripping section of the main solvent extraction system. The $U_3O_8$ combustion ash contains most of the uranium from the fuel since little is lost during delining. The $U_3O_8$ is dissolved in 6 M $HNO_3$ to produce a solution containing 300 g of uranium per liter. The uranium can be decontaminated and recovered from this solution by conventional TBP solvent extraction using stainless steel equipment similar to that at the Idaho Chemical Processing Plant.

With coated-particle Rover fuel elements, it is possible that the delining solution and washes will contain so little uranium that they can be discharged

directly to waste, particularly if delining is conducted at temperatures below the boiling point of the reagent. In the manufacture of the coated-particle elements, the propellant channels will probably be pretreated with gaseous HCl at high temperature to remove the uranium from any particles broken when the channels are reamed out; then, the NbC liner will be applied by vapor deposition. As a result, no uranium should be present in the liner as a UC-NbC solid solution prior to irradiation. If no uranium is dissolved during delining, dissolution of the $U_3O_8$ combustion ash in nitric acid can provide a fluoride-free solution containing 300 to 350 g of uranium per liter, which would be suitable as a feed for Purex-type solvent extraction methods.

Recovery of the niobium from the delining solution, for example, by extraction with hexone, is also possible (Sec. 2.4).

The DBD methods have several advantages over direct burning of the fuel element followed by $HNO_3$-HF dissolution of the ash. These are: (1) only about 8 moles of fluoride ion are required per mole of niobium for delining, whereas at least 60 moles of fluoride per mole of niobium are necessary for the dissolution of $Nb_2O_5$-$U_3O_8$ ash produced by combustion at 800 to 900°C (see Sec. 3.1); (2) elimination of the niobium prior to burning precludes the formation of clinkers caused by melting of $Nb_2O_5$ and the formation of $Nb_2O_5$-$U_3O_8$ solid solutions; and, (3) burning and dissolving can probably be conducted in the same stainless steel or Corronel vessel, thus obviating transfer of the combustion ash to a separate dissolver. If fused clinkers formed during combustion, their transfer would be difficult.

The DBD processes have several disadvantages: (1) Plastic vessels will be required to contain the highly corrosive $HNO_3$-HF solutions. Since radiation levels will be relatively low, no damage to the plastic is expected. The poor heat-transfer properties of plastics may be a severe problem. However, since the delining reaction is exothermic,transfer of heat into the vessel is probably not required. (2) The delined and washed fuel must be transferred to the burner, an operation which might present some engineering problems. However, the possibility of conducting the delining operation in easily transferable,and burnable plastic containers should not be

overlooked. (3) The temperature during burning must be carefully controlled to keep the wall temperature below 1000°C if excessive corrosion of the burner is to be avoided.

Preliminary engineering study of the DBD process has begun.[13] In the first experiments, clusters of about five, 27-in.-long Kiwi-BIA fuel rods (total weight, about 1.5 kg) were delined with 5 M HF--5 M $HNO_3$ (F/Nb mole ratio of about 10). More than 99.9% of the niobium was dissolved along with 10 to 20% of the uranium. The delined and washed fuel was burned in oxygen in a stainless steel vessel, and no excessive corrosion was noted. The $U_3O_8$ ash was dissolved in 6 M $HNO_3$. The uranium recovered in the delining solution and the 6 M $HNO_3$ solution was 99.4%.

## 2.2 Laboratory Demonstration of the DBD Flowsheet

Three laboratory-scale experiments were conducted with 35-g samples of unirradiated Kiwi-BIA fuel (which did not contain coated fuel particles) following the flowsheet conditions given in Fig. 1a. The delining equipment used is described in Appendix A. In each experiment, delining was initiated at 26°C, but the temperature increased to about 65°C during the first 8 to 10 min of the 6-hr delining period. The temperature then slowly returned to 26°C. The F/Nb mole ratios in these experiments were between 7.8 and 9.5 (Table 1). In each case, a small amount of nitric acid-insoluble residue remained after ash dissolution. This residue, which corresponded to less than 0.6% of the weight of the original sample, was mainly iron and niobic oxides and contained less than 0.09% of the total uranium (Table 1). The compositions of the solvent extraction feed solutions were about those expected (Table 2). The slight variations are due to the difference between the actual fuel composition and that used to calculate values for the flowsheet.

Several other DBD experiments with Kiwi-BIA fuel were conducted in which the delining conditions were varied. The procedure involved dissolution of the NbC liner in an HF-$HNO_3$ solution, washing the delined fuel with five portions of cold water (the volume of each portion was equal to the volume of the delining solution), burning the delined and washed fuel in oxygen for 5 to 6 hr at 800-1000°C, and dissolving the uranium oxide ash in 6 M $HNO_3$ ($HNO_3$/U mole ratio of about 6).

Table 1. Data from Deline-Burn-Dissolve Flowsheet Experiments with Kiwi-BIA Fuel Samples

(Conditions shown in flowsheet, Fig. 1a)

| Run No. | Fuel Comp.(%) U | Nb | Fe | F/Nb Mole Ratio | $HNO_3$ Insoluble Residue After Burning, (% of orig. sample) | Amounts Retained by Insoluble Residue (%) U | Nb | Fe |
|---|---|---|---|---|---|---|---|---|
| 84 | 17.9 | 9.6 | 0.25 | 7.8 | 0.54 | 0.08 | 0.28 | 78.6 |
| 85 | 18.1 | 7.7 | 0.09 | 9.5 | 0.17 | 0.08 | 0.33 | 53.1 |
| 86 | 18.2 | 8.0 | 0.10 | 9.2 | 0.11 | 0.03 | 0.02 | 44.4 |

Table 2. Solvent Extraction Feed Solutions for Deline-Burn-Dissolve Flowsheet Experiments

| Run No. | Feed Solution Composition (M) | | | |
|---|---|---|---|---|
| | Uranium | Niobium | HF | $HNO_3$ |
| Calculated | 0.074 | 0.125 | 1.00 | 3.00 |
| 84 | 0.100 | 0.137 | 1.07 | 3.45 |
| 85 | 0.103 | 0.113 | 1.07 | 3.45 |
| 86 | 0.103 | 0.116 | 1.07 | 3.45 |

Delining was virtually complete in a 4-hr period starting either at room temperature or at the boiling point, using a mixture that was 3 to 5 M in HF and 1 to 5 M in $HNO_3$ (Table 3). Only about 10% of the uranium was dissolved when the reaction was initiated at room temperature, but 25 to 35% was dissolved in boiling solutions. A residue consisting chiefly of $\gamma$-$Fe_2O_3$ (corresponding in weight to 0.2 to 0.3% of the weight of the fuel) remained after dissolution of the uranium oxide combustion ash in nitric acid. In the only case where analysis was possible, 0.32% of the uranium was found in this residue (Table 3). In earlier work,[4] it was shown that iron-bearing residues of this nature could be dissolved only when the nitric acid dissolvent contained about 1 M HCl, a condition which would necessitate a titanium dissolver. The iron content of the new coated-particle Rover fuels is expected to be less than 50 ppm so that it is probable that uranium losses to the nitric acid-insoluble residue formed during burning will be insignificant. In each of the experiments a corrosion coupon was placed in the burner adjacent to the fuel sample such that the coupon was contacted by the hot product gases from the combustion. This was done to determine whether the traces of fluoride remaining from the delining and washing steps would cause catastrophic corrosion of iron-base alloys during combustion. Coupons of Carpenter 20 and types 347 and 309 stainless steels were used in the three experiments. In each case, the coupon remained intact and exhibited only a slight weight gain.

Table 3. Additional Deline-Burn-Dissolve Experiments with Kiwi-BIA Fuel, Using Various Delining Conditions

Fuel composition: 16% uranium; 9% niobium; 0.1% iron
Fuel delined in $HNO_3$-HF solution and washed with 5 vols of water
Delined fuel burned in oxygen at 800-1000°C
$U_3O_8$ combustion ash dissolved in boiling 6 M $HNO_3$

| Run No. | Conc. in Delining Solution (M) HF | Conc. in Delining Solution (M) $HNO_3$ | F/Nb Mole Ratio | Temp. During Delining (°C) | Nb Left After Delining (%) | U Dissolved During Delining[a] (%) | Insoluble Residue After $HNO_3$ Diss. of Ash[b] (% of orig. fuel) | U Loss to $HNO_3$-Insol. Residue (%) |
|---|---|---|---|---|---|---|---|---|
| 38 | 5 | 5 | 26 | 25-30 | 0.0 | 10 | 0.34 | 0.32 |
| 25 | 3 | 1 | 16 | boiling | 0.02 | 25 | 0.24 | --- |
| 22 | 3 | 3 | 13 | boiling | 0.02 | 35 | 0.32 | --- |

[a] These high results are to be expected since the fuel did not contain coated fuel particles.

[b] X-ray analysis showed the residue to be mainly $\gamma$-$Fe_2O_3$.

## 2.3 Factors Affecting Delining

Experiments were conducted to determine the optimum conditions for dissolving the NbC liners in $HF-HNO_3$ solutions and washing the delined fuel, and to determine the amounts of fluoride which would be carried over to the combustion step. These experiments were conducted with Kiwi-BIA fuel specimens that did not contain coated particles. Conditions investigated were HF and $HNO_3$ concentrations, F/Nb mole ratio, and reaction temperature.

In a prior study,[4] it was shown that the highest initial rates of dissolution of NbC in $HF-HNO_3$ solutions were obtained when the $HNO_3$ concentration was in the range of 4 to 12 M and the HF concentration was greater than 1 M. In addition, subsequent work on the leaching of crushed Kiwi-BIA fuel[5] showed that an F/Nb mole ratio of at least about 10 was required for rapid dissolution of the NbC. These findings were generally borne out by the results of the present investigation (Table 4, Figs. 2 and 3).

In solutions where the HF concentration was greater than 1 M, the nitric acid concentration had the greatest effect on the amount of liner dissolved in a given digestion period. For example, in a 4-hr digestion with boiling solutions containing 1 to 5 M HF (F/Nb mole ratios of 8 to 15), the amount of NbC remaining in the fuel decreased from 100 to 0.1% as the $HNO_3$ concentration in the reagent increased from 0 to 3 M (Fig. 2). Other conditions being the same, the amount of NbC dissolved in the 4-hr period was increased slightly when the F/Nb mole ratio was increased to 25 to 60 (compare data given in Figs. 2 and 3). With boiling solutions, increasing the reaction time from 4 to 6 hr had little effect on the amount of NbC dissolved.

The NbC liners could be dissolved at about room temperature as well as at the boiling point. Again, nitric acid concentration was the most important variable when the HF concentration was greater than 1 M (Table 4, Figs. 2 and 3); delining was inadequate in solutions where the $HNO_3$ concentration was less than about 3 M (Table 4). Reaction time was more important in the low-temperature delining experiments than in those conducted with boiling solutions. An increase in reaction time from 4 to 6 hr resulted in the dissolution of about an additional 0.4% of the niobium at the lower temperatures (Table 4, Fig. 2). To maintain the reaction temperature near 25°C,

Table 4. Delining of Kiwi-BIA Fuel with $HNO_3$-HF Solutions

5 water washes after delining

| Run No. | Solution Conc. (M) HF | Solution Conc. (M) $HNO_3$ | Fuel Comp. (%) U | Fuel Comp. (%) Nb | F/Nb Mole Ratio | Temp. Increase (°C) | Reaction Time (hr) | Amounts Retained by Residue (%) U | Amounts Retained by Residue (%) Nb | $F^-$ Conc. in Residue (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 1 | 16.2 | 8.74 | 14.7 | 25-? | 4 | 98.9 | 97.1 | 0.21 |
| 2 | 5 | 1 | 16.7 | 9.22 | 12.7 | 25-? | 4 | 93.7 | 84.8 | 0.17 |
| 3 | 3 | 3 | 18.1 | 9.05 | 13.7 | 25-? | 4 | 83.2 | 0.75 | 0.0099 |
| 4 | 3 | 3 | 16.3 | 8.61 | 13.9 | 25-? | 4 | 90.4 | 0.91 | 0.027 |
| 5 | 1 | 5 | 20.6 | 7.36 | 11.4 | 25-28 | 4 | 88.2 | 0.16 | 0.03 |
| 6 | 5 | 5 | 16.9 | 8.13 | 14.5 | 25-? | 4 | 90.5 | 0.32 | 0.066 |
| 7 | 2 | 15 | 19.4 | 6.38 | 15.7 | 25-? | 4 | 92.0 | 0.12 | 0.035 |
| 8 | 3 | 1 | 17.8 | 9.12 | 8.8 | 25-26 | 6 | 95.0 | 92.1 | 0.27 |
| 9 | 5 | 1 | 18.0 | 9.42 | 10.1 | 25-29 | 6 | 86.9 | 79.4 | 0.15 |
| 10 | 3 | 2 | 17.8 | 8.33 | 9.6 | 25-28 | 6 | 88.7 | 19.4 | 0.057 |
| 11 | 5 | 3 | 17.6 | 9.04 | 10.8 | 25-55 | 6 | 87.2 | 0.10 | 0.13 |
| 12 | 5 | 5 | 17.9 | 8.30 | 12.1 | 25-67 | 6 | 89.0 | 0.073 | 0.09 |
| 13 | 3 | 10 | 17.6 | 8.99 | 8.9 | 25-65 | 6 | 92.3 | 0.059 | 0.032 |
| 14 | 3 | 15 | 17.5 | 8.98 | 8.7 | 25-65 | 6 | 92.1 | 0.050 | 0.034 |
| 15 | 5 | 5 | 16.2 | 7.70 | 60.3 | 25-31 | 4 | 88.9 | 0.24 | 0.16 |
| 16 | 5 | 5 | 16.7 | 9.16 | 25.0 | 25-39 | 4 | 89.9 | 0.11 | 0.05 |
| 17 | 5 | 5 | 18.2 | 7.09 | 64.6 | 25-31 | 4 | 89.6 | 0.16 | 0.11 |
| 18 | 2 | 10 | 19.0 | 3.80 | 24.3 | 25-? | 4 | 93.6 | 0.20 | 0.026 |
| 19 | 3 | 0.5 | 17.3 | 8.67 | 14.3 | b.p. | 4 | 80.2 | 48.3 | 0.47 |
| 20 | 5 | 0.5 | 17.9 | 9.23 | 12.0 | b.p. | 4 | 84.2 | 63.2 | 1.2 |
| 21 | 1 | 1 | 16.9 | 7.91 | 12.8 | b.p. | 4 | 54.7 | 0.57 | 0.09 |
| 22 | 2 | 1 | 17.5 | 8.31 | 12.0 | b.p. | 4 | 54.8 | 1.07 | 0.18 |
| 23 | 3 | 1 | 16.8 | 8.82 | 14.5 | b.p. | 4 | 78.9 | 0.76 | 0.13 |
| 24 | 3 | 1 | 18.3 | 9.00 | 13.7 | b.p. | 4 | 68.0 | 0.60 | 0.17 |
| 25 | 5 | 1 | 17.2 | 8.98 | 12.4 | b.p. | 4 | 63.8 | 11.8 | 0.52 |
| 26 | 1 | 3 | 17.1 | 8.86 | 11.0 | b.p. | 4 | 44.1 | 0.11 | 0.066 |
| 27 | 2 | 3 | 17.6 | 8.50 | 12.8 | b.p. | 4 | 47.8 | 0.11 | 0.10 |
| 28 | 3 | 3 | 16.7 | 8.90 | 13.4 | b.p. | 4 | 64.4 | 0.22 | 0.12 |
| 29 | 3 | 5 | 17.8 | 8.92 | 9.0 | b.p. | 4 | 80.9 | 0.058 | 0.43 |
| 30 | 1 | 10 | 17.2 | 8.64 | 9.0 | b.p. | 4 | 44.4 | 0.043 | 0.05 |
| 31 | 3 | 10 | 15.8 | 9.34 | 8.7 | b.p. | 4 | 61.2 | 0.084 | 0.15 |
| 32 | 2 | 15 | 18.0 | 8.67 | 10.5 | b.p. | 4 | 69.7 | 0.05 | 0.09 |
| 33 | 3 | 1 | 18.5 | 8.61 | 14.4 | b.p. | 6 | 47.1 | 0.12 | 0.29 |
| 34 | 3 | 3 | 18.4 | 8.81 | 14.1 | b.p. | 6 | 51.2 | 0.090 | 0.33 |
| 35 | 3 | 0.5 | 17.0 | 7.46 | 33.4 | b.p. | 4 | 54.0 | 1.35 | 0.25 |
| 36 | 5 | 0.5 | 17.4 | 6.81 | 32.7 | b.p. | 4 | 45.0 | 9.26 | 0.30 |
| 37 | 3 | 1 | 19.4 | 10.1 | 24.6 | b.p. | 4 | 58.8 | 0.074 | 0.30 |
| 38 | 5 | 1 | 17.6 | 9.06 | 24.5 | b.p. | 4 | 47.9 | 0.070 | 0.43 |
| 39 | 3 | 3 | 17.8 | 9.21 | 27.0 | b.p. | 4 | 58.8 | 0.045 | 0.16 |
| 40 | 3 | 5 | 17.8 | 8.94 | 17.8 | b.p. | 4 | 77.8 | 0.039 | 0.13 |
| 41 | 3 | 10 | 17.2 | 8.87 | 17.3 | b.p. | 4 | 94.5 | 0.060 | 0.03 |
| 42 | 5 | 1 | 15.3 | 9.03 | 26.6 | b.p. | 6 | 57.3 | 0.060 | 0.59 |
| 43 | 5 | 1 | 17.7 | 10.0 | 45.7 | b.p. | 6 | 48.4 | 0.062 | 0.39 |

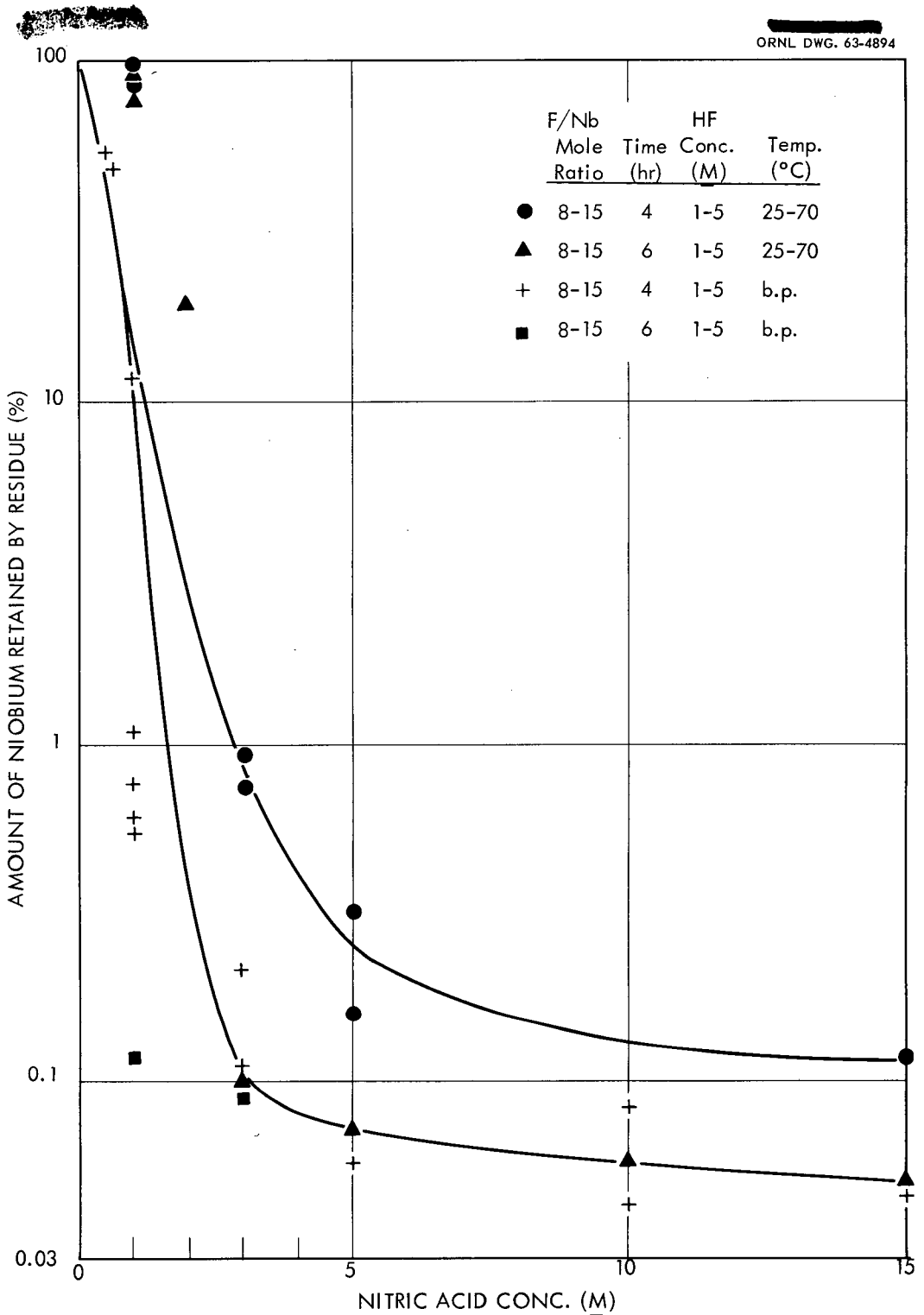


Fig. 2. Effect of Temperature, Time, and Nitric Acid Concentration on the Delining of KIWI-B1 Fuel Samples in $HNO_3$-HF Solutions in Experiments where the Overall F/Nb Mole Ratios were 8-15.

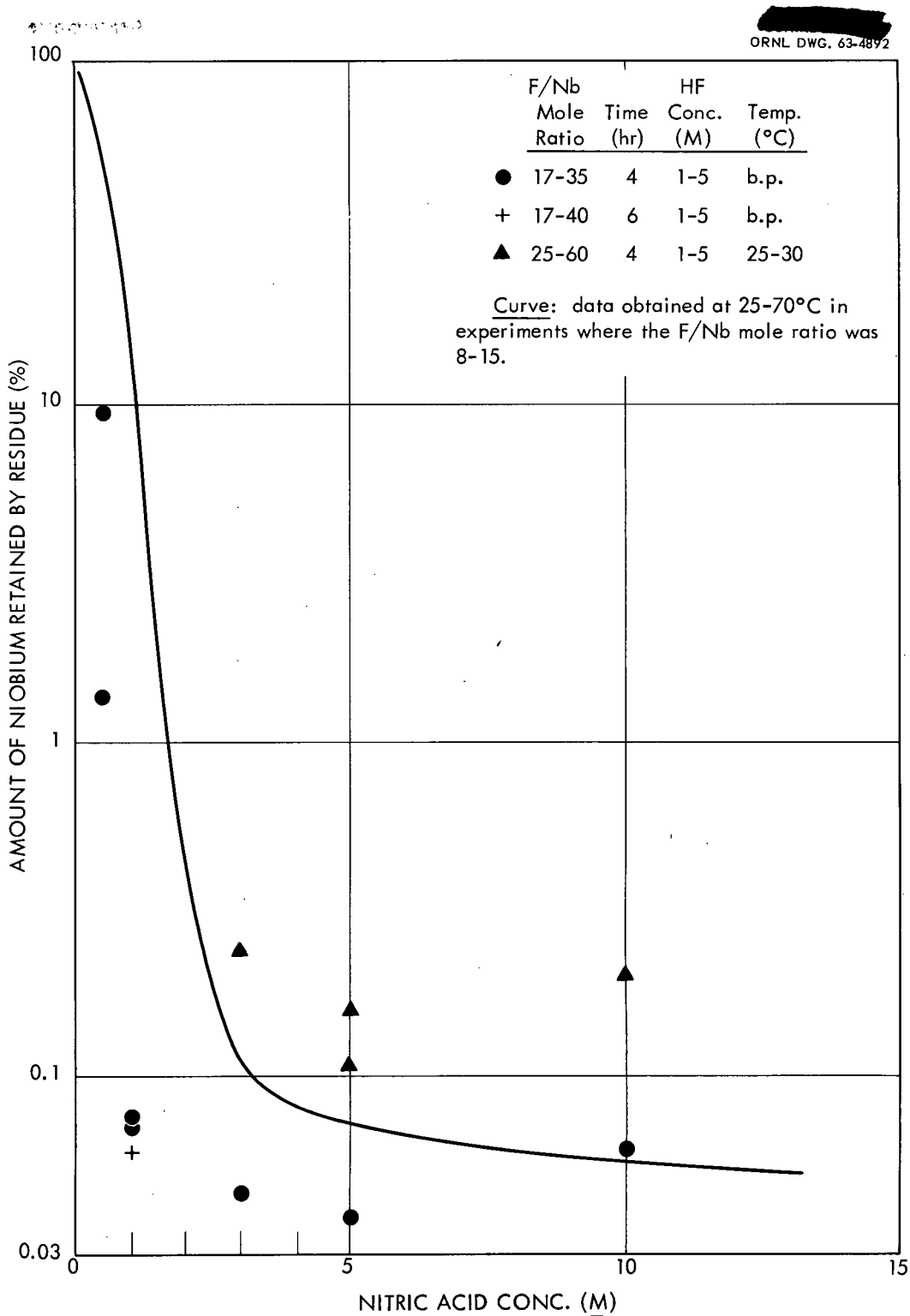


Fig. 3. Effect of Time and Temperature on the Delining of KIWI-B1 Fuel Samples in $HNO_3$-HF Solutions in Experiments where the Overall F/Nb mole Ratio was greater than 17.

large solution volumes (indicated by F/Nb mole ratios of 25 to 60) were required to absorb the heat of reaction (Table 4, runs 15-18). In solutions of minimal volume (F/Nb mole ratios of 8 to 15), the temperature rose as high as 70°C (Table 4, runs 11-14) in the apparatus used (Appendix A). Nevertheless, for two reasons, initiating the delining reaction at room temperature might be more practical than using boiling reagents. First, the necessity for heating the plastic vessel required to contain $HF-HNO_3$ solutions would be obviated. Secondly, since less uranium is dissolved at the lower temperatures (Table 4), low-temperature delining of coated-particle fuel might result in insignificant losses of uranium to the delining solution.

In each experiment, the delined fuel was washed with water at room temperature to remove residual solution. After 3 to 5 washes (each being equal in volume to the delining solution), the fluoride content of the delined fuel was generally reduced to less than 0.5% (Table 4). This amount of fluoride had no marked effect on the corrosion of stainless steels in burning experiments (Sec. 2.2) or on Corronel 230 in systematic flowsheet corrosion studies (Sec. 2.5).

## 2.4 Recovery of Niobium from Delining Solutions

Irrespective of the uranium content of the delining solutions, it might be economically attractive to recover the niobium before further treatment of the solutions. One method for recovering niobium from $HF-HNO_3$ solutions is extraction with hexone (methyl isobutyl ketone).[14]

Solutions, with HF concentrations varying from 2 to 7 M and with $HNO_3$ concentrations varying from 2 to 8 M, containing 22 ± 3 g of niobium per liter and less than 3 ± 1 g of uranium per liter, were prepared by delining sections of Kiwi-BIA fuel. Each solution was equilibrated at 26°C with an equal volume (5 ml) of hexone for 2 min before the phases were separated and analyzed. Extraction coefficients ($E_a^o$ = conc. in hexone/conc. in aqueous) were determined for both niobium and uranium. The data (Table 5 and Fig. 4) show that in solutions where the HF concentration was 6 to 7 M, the extraction coefficient for niobium was 0.4 to 0.5 while that for uranium was less than 0.03.

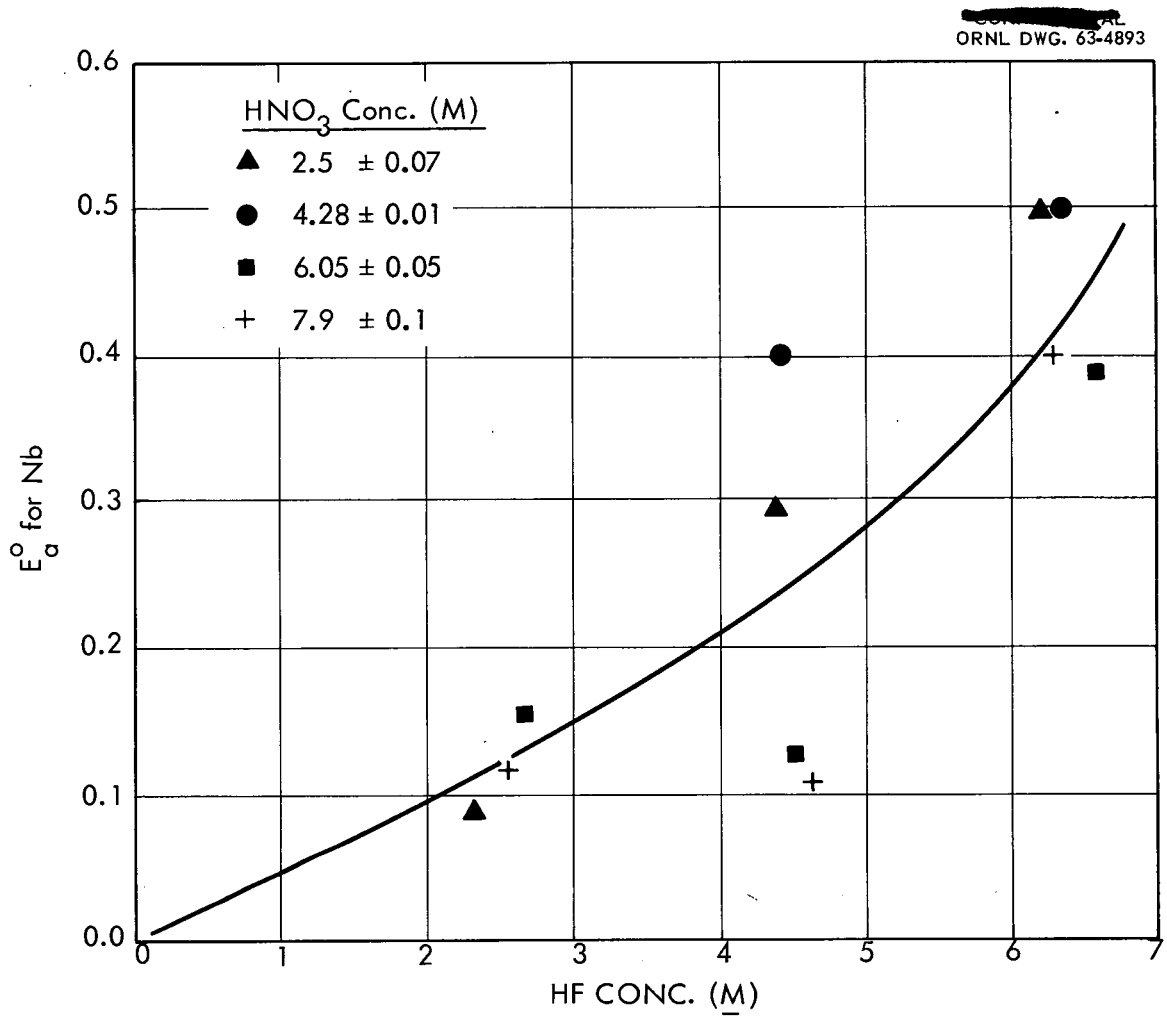


Fig. 4. Effect of HF and $HNO_3$ Concentrations on the Extraction of Niobium from HF-$HNO_3$ Solutions with Hexone at 26°C. Equal volumes (5 ml) of aqueous and organic phases were equilibrated for 2 min. Each aqueous solution originally contained 22 ± 3 g of Nb per liter and 3 ± 1 g of U per liter.

The niobium extraction data agree qualitatively with those given in the literature[14] and show that niobium can probably be recovered from delining solutions of low uranium concentration by means of multistage extraction. Furthermore, since the separation of niobium from uranium was reasonably good (Table 5), alternative DBD flowsheets are suggested. In the event that no significant loss of uranium

Table 5. Extraction of Niobium and Uranium from HF-$HNO_3$ Delining Solutions with Hexone

Each solution contained 22 ± 3 g of niobium per liter and less than 3 ± 1 g of uranium per liter; 5 ml each of hexone and aqueous solution were equilibrated for 2 min before analysis

| Sample | Conc. (M) | | $E_a^\circ$ at 26°C | |
|---|---|---|---|---|
| | $HNO_3$ | HF | Niobium | Uranium |
| 1 | 2.43 | 2.32 | 0.094 | 0.006 |
| 2 | 6.08 | 2.62 | 0.16 | 0.059 |
| 3 | 7.95 | 2.55 | 0.12 | 0.028 |
| 4 | 2.48 | 4.38 | 0.30 | 0.003 |
| 5 | 4.29 | 4.42 | 0.40 | 0.019 |
| 6 | 6.10 | 4.50 | 0.13 | 0.026 |
| 7 | 7.97 | 4.63 | 0.11 | 0.0008 |
| 8 | 2.58 | 6.18 | 0.50 | 0.036 |
| 9 | 4.26 | 6.34 | 0.50 | 0.022 |
| 10 | 6.05 | 6.55 | 0.39 | 0.027 |
| 11 | 7.82 | 6.28 | 0.40 | 0.002 |

to the $HNO_3$-HF solutions occurs during delining, both uranium and niobium could possibly be recovered from Rover fuel by using the process shown schematically in Fig. 5. Delining would be conducted in a plastic vessel by using a solution containing about 5 M $HNO_3$ and 10 M HF. The fuel would then be washed with about an equal volume of water; the wash solution would be combined with the

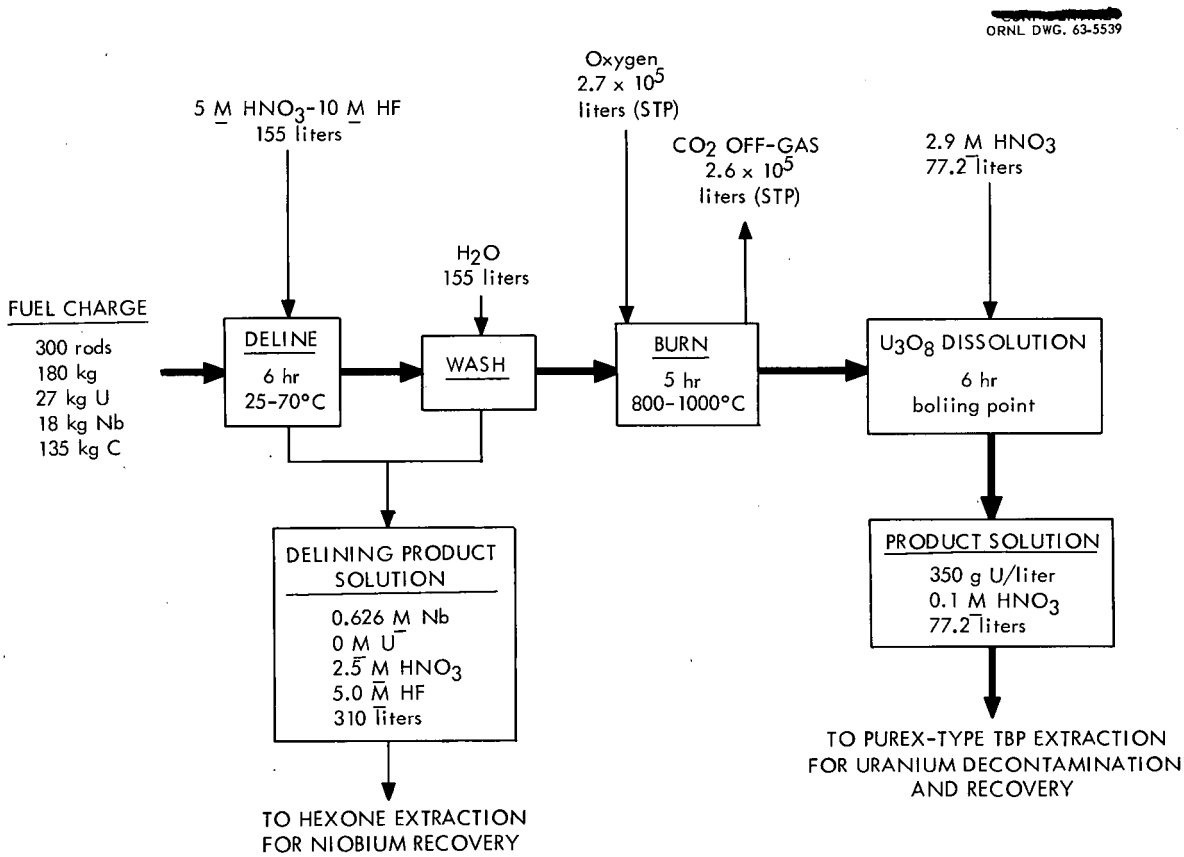


Fig. 5. Suggested Alternative DBD Process for Recovery of Both Uranium and Niobium from Coated-Particle Rover Fuel in the Event that No Uranium is Lost to the Delining Solution.

delining solution. Niobium would be recovered from this combined solution by extraction with hexone, and the raffinate would be discarded to waste. The delined and washed fuel (containing virtually all the uranium originally present in the fuel) would be burned and the $U_3O_8$ ash dissolved in boiling nitric acid to produce a Purex-type solvent extraction feed solution containing about 350 g of uranium per liter and essentially no free hydrogen ion.

In the case where a significant amount of uranium is lost to the delining solution, the niobium can be removed from the delining solution with hexone before proceeding with the DBD flowsheet conditions given in Fig. 1.

## 2.5 Corrosion Studies Relating to the Deline-Burn-Dissolve Process*

Metallic vessels probably cannot be used to contain the delining solution because of the high hydrofluoric acid concentration, greater than 1 M, required to dissolve the NbC (Sec 2.3). For example, Corronel 230 alloy corroded catastrophically[15] in 0 to 10 M $HNO_3$ containing 0.3 to 5 M HF. Stainless steels, type 304L and similar alloys, were unsuited[16] for use in boiling 2 to 10 M $HNO_3$ containing more than 1 M HF. Based on experiments in this Laboratory, Teflon would make an excellent container for the strong $HNO_3$-HF solutions required for delining.

Several metallic alloys were tested in an oxidation-nitric acid dissolution cycle to simulate the burning of delined and washed Rover fuel. Corronel 230 appeared to be the best of the materials tested, being corroded at a rate of less than 0.1 mil/month over 22 cycles. Coupons of candidate materials were buried in a paste of graphite and $UO_2$ which was wet with sufficient HF-$HNO_3$ solution to adjust the fluoride and nitrate contents of the mixture to 0.5 and 1.5%, respectively. Then the mixture was burned in oxygen at about 800°C for 5 hr, and the ash was dissolved in boiling 5 M $HNO_3$ in 2.5 hr in the presence of the coupon. Each coupon was weighed and examined between cycles. In addition to Corronel 230, the following alloys were tested in the oxidation-dissolution cycle: "A" nickel, Carpenter 20, Haynes 25, Nichrome V, and 304L stainless steel. Other than Corronel 230, none of the metals was sufficiently resistant to corrosion:

* The authors are indebted to L. Rice, D. N. Hess, and P. D. Neumann, ORNL Reactor Chemistry Division, and W. E. Clark, Chemical Technology Division, for obtaining these corrosion results.

| Alloy | No. of Cycles | Average Corrosion Rate (mils/month) | Remarks |
|---|---|---|---|
| Corronel 230 | 22 | 0.1 | --- |
| "A" Nickel | 1 | 6000 | Specimen dissolved |
| Nichrome V | 9 | 22 | --- |
| 304L stainless steel | 7 | 15-20 | Grain-boundary attack |
| Haynes 25 | 17 | 8 | Intergranular attack |
| Carpenter 20 | 17 | 5 | Intergranular attack |

Extraction of the uranium from the DBD feed solution (1 M HF, 3 to 4 M $HNO_3$) possibly can be conducted in type 309SCb stainless steel at room temperature. Extrapolation of SRL data [15,16] indicates that this alloy would be corroded at a rate of 1 to 10 mils/month during the extraction.

## 3. DEVELOPMENT OF THE BURN-DISSOLVE PROCESS

The Burn-Dissolve process involves combustion of the entire fuel element (perhaps after crushing), transfer of the combustion ash to a plastic dissolver, and dissolution of the ash in boiling $HNO_3$-HF solution. The uranium is recovered from the product solution by the same extraction technique used in the DBD process.

### 3.1 Tentative Burn-Dissolve Flowsheet

The first step in the tentative flowsheet (Fig. 6) is burning of the fuel in oxygen for 5 hr at 800 to 1000°C. The $U_3O_8$-$Nb_2O_5$ ash must be transferred to a plastic vessel for dissolution because no suitable material has been found which can withstand the corrosion over the combustion-dissolution cycle. The ash is dissolved in boiling $HNO_3$-HF solution; the F/Nb mole ratio must be at least 60 to ensure complete dissolution.[5] Dissolution of the ash is best accomplished in solutions containing at least 2 M $HNO_3$ and 1 M HF (ref. 5). The dissolvent given in the flowsheet (Fig. 6) is 4 M $HNO_3$--1 M HF since these appear to be the optimal

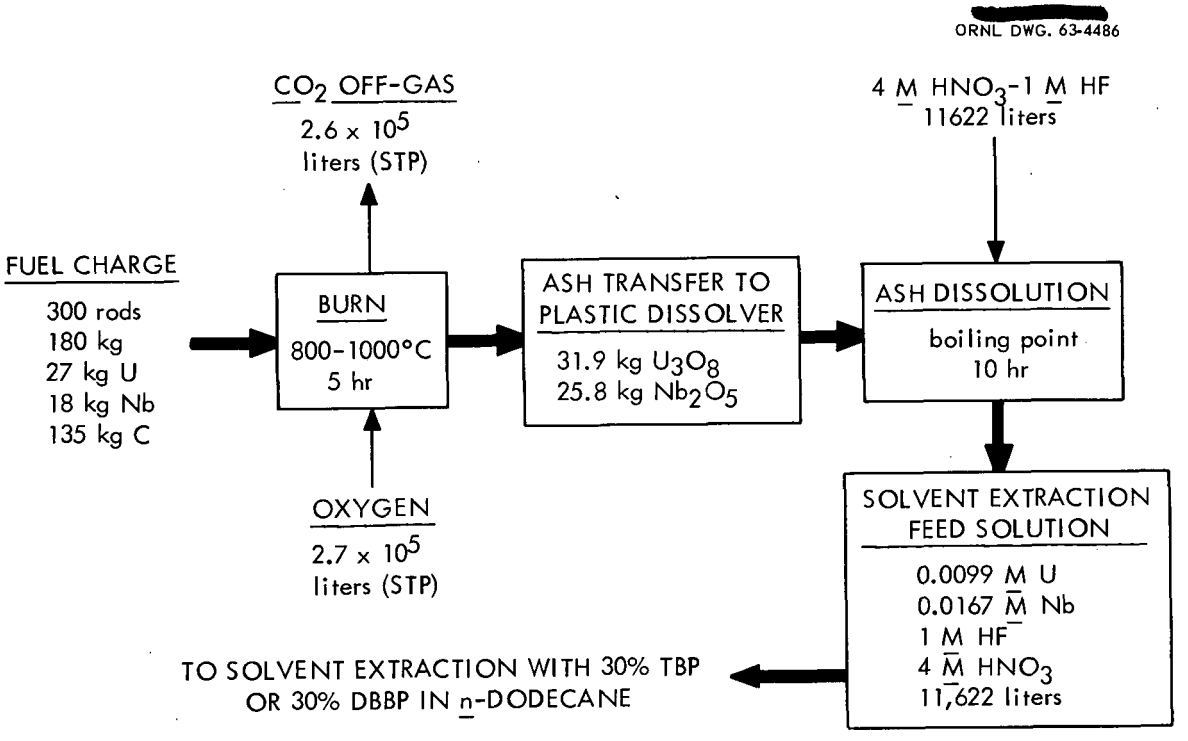


Fig. 6. Tentative Burn-Dissolve Process for Coated-Particle Rover Fuels.

acid concentrations for solvent extraction.[12] Uranium can be decontaminated and recovered from the solvent extraction feed solution using either TBP or DBBP.

If the Burn-Dissolve process has any advantages over the DBD process, they are that the engineering problems associated with transferring a batch of delined fuel to the burner are avoided,and vessels for storing the delining solution until ash dissolution is complete are not needed. The chief disadvantages are that a transfer of the combustion ash must be made and that the F/Nb mole ratio must be at least 60 to effect complete dissolution. This is 8 times as much fluoride as required in the DBD process (Sec 2.1). The presence of both uranium and niobium during combustion makes careful temperature control mandatory to avoid the formation of clinkers of $U_3O_8$-$Nb_2O_5$ solid solution. These clinkers form readily due mainly to the low melting point of $Nb_2O_5$ (1460°C, ref. 17). Clinker formation not only will make the transfer of the ash difficult, but will also make the ash more difficult to dissolve.

## 3.2 Factors Affecting Dissolution of the Combustion Ash

### 3.2.1 Effect of Nitric and Hydrofluoric Acid Concentrations

Dissolution of the $U_3O_8$-$Nb_2O_5$ combustion ash is best accomplished in boiling $HNO_3$-HF solutions when the HF concentration is greater than 1 molar.[5] In experiments with ash from fuel burned at 800 to 900°C, an F/Nb mole ratio of at least 60 was required to effect complete dissolution, even in dissolving times of up to 24 hr (ref. 5). Variations in the nitric acid concentration between 1 and 21 M had little effect on the extent of dissolution.[5] With Kiwi-BIA fuel (which did not contain coated fuel particles), complete uranium recovery was achieved only by completely dissolving the ash; that is to say, the uranium could not be leached from the ash with nitric acid alone. Up to 5% of the uranium was lost to the insoluble $Nb_2O_5$ residue when the ash was leached only with nitric acid.[5]

### 3.2.2 Effect of Sintering Temperature on the Dissolution of $Nb_2O_5$ in HF-$HNO_3$ Solutions

Preliminary experiments to determine the effect of burning (or sintering) temperature on the dissolution of the ash were conducted in an effort to establish temperature

limitations for the burning of lined Rover fuel. The sintering temperature had a pronounced effect on the dissolubility of $Nb_2O_5$. As expected, the higher the sintering temperature, the more refractory the oxide produced.

In tests with freshly precipitated hydrated $Nb_2O_5$, which had been partially dried at 80°C, complete dissolution was achieved in 3 hr at room temperature in 1 to 20 M $HNO_3$ solutions containing 0.2 to 2 M HF, with an overall F/Nb mole ratio of only 10 (Table 6). On the other hand, after the $Nb_2O_5$ had been sintered at 800°C for 16 hr, it generally could not be dissolved in the same series of boiling dissolvents in a 3-hr period, even when the F/Nb mole ratio was 40 (Table 6). However, the sintered oxide could generally be dissolved in 16 hr in solutions

Table 6. Dissolution Tests with Hydrated, Sintered, and Fused $Nb_2O_5$

| Soln. Conc. (M) | | F/Nb Mole Ratio= | Dissolution Behavior[a] of Hydrated $Nb_2O_5$[b] | Sintered $Nb_2O_5$[c] | | | Fused $Nb_2O_5$[c] |
|---|---|---|---|---|---|---|---|
| $HNO_3$ | HF | | 10 | 10 | 40 | 60 | 40 |
| 1 | 0.2 | | cd 3 | id 3 | -- | -- | -- |
| 1 | 1.0 | | cd 3 | id 3 | id 3 | -- | -- |
| 3 | 0.5 | | cd 3 | -- | -- | -- | -- |
| 3 | 1.0 | | cd 3 | -- | id 16 | -- | -- |
| 5 | 1.0 | | cd 3 | -- | cd 16 | cd 16 | id 96 |
| 5 | 2.0 | | cd 3 | -- | id 3 | -- | -- |
| 10 | 1.0 | | cd 3 | id 16 | cd 3 | -- | cd 96 |
| 20 | 1.0 | | cd 3 | id 3 | -- | -- | -- |

[a] cd = complete dissolution; id = incomplete dissolution; numbers are dissolution times in hr; thus, cd 3 = complete dissolution in 3 hr.

[b] This series of experiments was conducted at room temperature.

[c] These experiments were conducted with boiling solutions.

where the $HNO_3$ concentration was greater than about 5 M provided that the F/Nb mole ratio was 40 or higher. For comparison, the dissolution of fused $Nb_2O_5$ in boiling 10 M $HNO_3$--1 M HF and 5 M $HNO_3$--1 M HF was studied cursorily. In the solution containing 10 M $HNO_3$, complete dissolution at a F/Nb mole ratio of 40 was achieved only after four days; whereas dissolution was incomplete in the solution containing only 5 M $HNO_3$ (Table 6). These tests, although preliminary, point out the need for careful temperature control in the burning of lined Rover fuel to avoid formation of a highly refractory ash. The fused $Nb_2O_5$ was obtained by heating hydrated $Nb_2O_5$ in a platinum boat at 1550°C for a few minutes, then allowing the molten mass to cool slowly overnight. X-ray analysis showed the fused oxide to be $\gamma$-$Nb_2O_5$.

### 3.2.3 Effect of Sintering Temperature on the Dissolution of $U_3O_8$-$Nb_2O_5$ Mixtures

The effect of sintering temperature on the dissolution in boiling HF-$HNO_3$ solutions of Kiwi-BIA combustion ash (45% uranium, 30% niobium) was studied briefly. In one series of tests, ash produced by combustion of fuel samples at 800 to 1000°C was used. For another series, the ash was melted at about 1500°C and completely fused by heating at 1550°C for 10 min. The ash lost only 1% of its weight on fusion and formed a black, brittle glass. X-ray analysis showed the fused melt to be a solid solution of $U_3O_8$ and $Nb_2O_5$. The fused ash was ground until it passed a 50-mesh screen prior to its use in the dissolution tests.

The experimental results showed that, as expected, the fused ash was more difficult to dissolve than the ash produced at the lower temperature (Table 7). In 16-hr tests with volumes of boiling solutions necessary to yield F/Nb mole ratios of 60, dissolution of the low-temperature ash was virtually complete in each of the HF-$HNO_3$ solutions used. On the other hand, up to 15% of the fused ash remained undissolved. However, the fused ash was completely dissolved in 16 hr in boiling 3 M $HNO_3$--5 M HF and 10 M $HNO_3$--1 M HF (Table 7). In general, the extent of dissolution of both the low-temperature and fused ash was increased by increasing the nitric acid concentration in solutions of constant hydrofluoric acid concentration and by increasing the hydrofluoric acid concentration in solutions of constant nitric

acid concentration. These preliminary data indicate that a Burn-Dissolve process for Rover fuel might be practical even if fusion of the ash does occur, provided that the ash can be easily transferred and powdered prior to dissolution.

Table 7. HF-$HNO_3$ Dissolution Experiments with Low-Temperature and Fused Kiwi-BIA Combustion Ash (45% U, 30% Nb)

Low-temperature ash obtained by burning fuel at 800 to 1000°C
Fused ash obtained by heating to 1550°C for 10 min
Dissolution time: 16 hr in boiling solution

| Dissolvent[a] | | Amount of Ash Remaining (%) | |
|---|---|---|---|
| HF (M) | $HNO_3$ (M) | Low-Temperature | Fused |
| 3 | 1 | 0.0 | 9.0 |
| 5 | 1 | 0.0 | 0.2 |
| 3 | 3 | 0.02 | 0.9 |
| 5 | 3 | 0.0 | 0.0 |
| 1 | 5 | 0.2 | 15. |
| 1 | 10 | 0.0 | 0.0 |

[a]F/Nb ratio in each experiment was 60.

### 3.3 Semicontinuous Dissolution of Combustion Ash

In an effort to dissolve 800°- to 1000°-combustion ash, using an overall F/Nb mole ratio lower than 60, a series of 4-hr experiments was conducted in which 3.45-g samples of ash were dissolved in boiling 4 M $HNO_3$--1 M HF on a semicontinuous basis. At the end of each 4-hr cycle, the product solution was replaced by a fresh volume of reagent and another 3.45-g charge of ash was added to the dissolver. The build-up of insoluble material (i.e., the "heel") and the concentrations in the product solution were determined over five cycles. The F/Nb mole ratio was 10 in the first cycle but decreased to about 3 in the fifth. The uranium concentration in each of the five product solutions was about 0.054 M, but the niobium concentration increased regularly from 0.05 to 0.08 M over the five cycles (Table 8). Since the nitric acid and hydrofluoric acid concentrations did not change appreciably during the dissolutions, each product solution was probably acceptable as a feed for solvent extraction.

Table 8. Semicontinuous Dissolution of Kiwi-BIA Combustion Ash in Boiling 4 M $HNO_3$--1 M HF

Conditions: Ash composition, 46.3% U; 25.8% Nb
Each cycle, 4 hr
Product solution replaced by fresh dissolvent and 3.45 gram of ash added at end of each cycle
F/Nb mole ratio, 10 in first cycle but decreased to about 3 over 5 cycles

| Cycle | Amount of Solids Dissolved (%) | Weight of Residue (g) | Conc. in Product Soln. (M) Uranium | Niobium |
|---|---|---|---|---|
| 1 | 61.6 | 1.32 | 0.054 | 0.053 |
| 2 | 51.2 | 2.33 | 0.054 | 0.067 |
| 3 | 44.0 | 3.23 | 0.053 | 0.061 |
| 4 | 37.7 | 4.16 | 0.056 | 0.072 |
| 5 | 36.8 | 4.81 | 0.058 | 0.076 |

The amount of insoluble material (which was becoming increasingly rich in niobium) increased steadily over the five cycles (Fig. 7). Nevertheless, a semicontinuous dissolution technique probably would require much less HF than successive batch total dissolutions since the "heel" could be allowed to accumulate over many cycles before its complete dissolution would be necessary.

## 4. DEVELOPMENT OF THE BURN-LEACH PROCESS

As mentioned earlier (Sec. 2.1), before applying the NbC liner to the new coated-particle Rover fuel elements the coolant channels will probably be treated with HCl gas at high temperature to remove the uranium from any particles broken when the channels are reamed out. If this is done, it is possible that little or no uranium will migrate into the NbC liners during reactor operation. Since the amount of uranium present in the liner correlates well with the amount of uranium lost to the insoluble $Nb_2O_5$ combustion residue after leaching with nitric acid

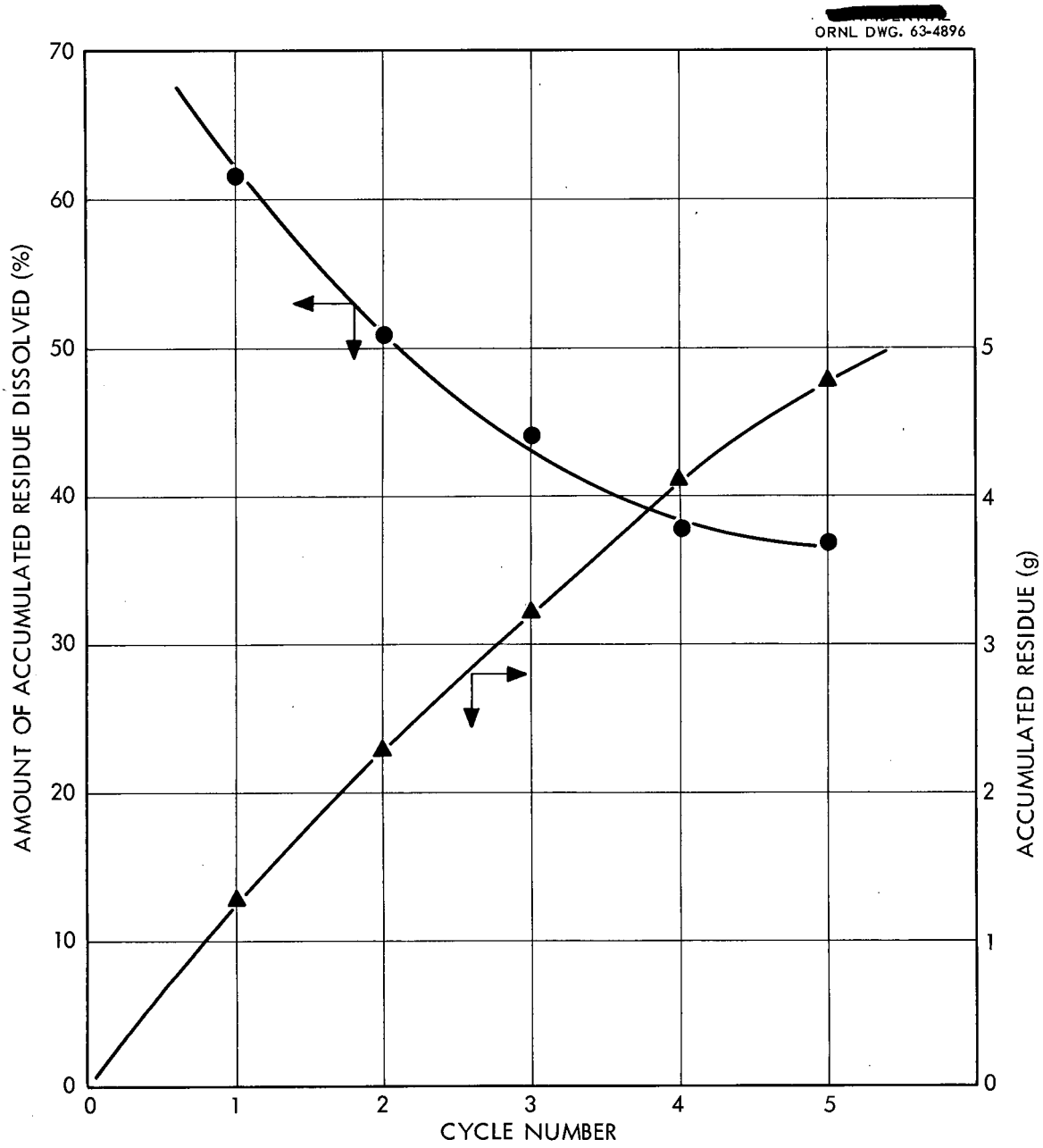


Fig. 7. Build-Up of Residue During 5-Cycle Experiment in which Rover Combustion Ash was Dissolved in Boiling 1 M HF--4 M $HNO_3$. A fresh charge of 3.45 g of ash was added at the start of each cycle along with 100 ml of fresh reagent. F/Nb mole ratio in each cycle was 5 to 10.

alone,[5] with the new fuels it is possible that a nitric acid leach after burning will result in adequate uranium recovery, leaving only $Nb_2O_5$ in the waste.

The Burn-Leach process would, therefore, involve burning of the fuel at a controlled temperature in stainless steel or Corronel equipment followed by leaching of the uranium from the ash with boiling nitric acid in the same equipment. The product solution would necessarily have to be separated from the insoluble $Nb_2O_5$ residue by either filtration or centrifugation. Two laboratory experiments were conducted to test this procedure with samples of prototype 19-hole Kiwi-B6A fuel which did contain coated fuel particles. The fuel contained 17% uranium and 7% niobium. The samples were burned in oxygen at 800 to 1000°C for 6 hr; the ash was then leached for 5 hr with boiling 6 M $HNO_3$ to produce a solution containing 1.4 M uranium and about 4 M $HNO_3$. The solution was separated from the insoluble $Nb_2O_5$ by vacuum filtration. The insoluble residues contained only about 0.6% of the uranium in both experiments. The product solutions contained only about 0.05% of the niobium. These results indicate that the Burn-Leach method might be practicable with coated-particle Rover fuels, so more experiments are planned.

## 5. GRIND-LEACH PROCESS

Another potential aqueous process for coated-particle Rover fuel is fine grinding followed by nitric acid leaching to recover the uranium. This process would obviate the need for burning the fuel but would introduce the problems associated with fine grinding and separation of the product solution from the powdered graphite. No work has been conducted on this process as yet due to the unavailability of coated-particle Rover fuel. However, in tests with other types of graphite-base fuels containing coated particles,[18,19] uranium recoveries were almost quantitative once the fuel was ground fine enough to ensure rupture of all the fuel particles. For Rover fuels, this would mean grinding to about 200 mesh. The Grind-Leach process using only nitric acid would be inapplicable to Rover fuel, if, during reactor operation, more than 0.1% of the uranium diffused into the NbC liner. UC-NbC solid solutions of

high NbC content behave almost like pure NbC and cannot be dissolved in $HNO_3$ alone.[4,5] If more than 0.1% of the uranium diffused into the liner, the powdered fuel could be leached with $HF-HNO_3$ solutions to achieve the desired uranium recovery.

Assuming that no uranium is associated with the NbC liner and that fine grinding and leaching can be accomplished, it might be possible to extract the uranium directly from the graphite-leach solution slurry.[20]

## 6. SUPPORTING CHEMICAL STUDIES

### 6.1 Solubility of Niobium in $HF-HNO_3$ and HF Solutions

In support of the process development, the solubility of $Nb_2O_5$ in HF and $HF-HNO_3$ solutions at 25°C is being determined. Preliminary results show that irrespective of the nitric acid concentration between 0 and 21 M, the niobium concentration in the saturated solution is about 1/5 the HF concentration (Table 9, Fig. 8). This observation is in agreement with the reaction $Nb_2O_5 + 10HF \longrightarrow 2H_2NbOF_5 + 3H_2O$. The solution analyses obtained in HF solutions are in general agreement with those published by others.[21] However, the appearance of $NbO_2F \cdot 1/2\ H_2O$ as a solid phase has been observed and, therefore, similar solubility measurements starting with this material are in progress in an effort to approach equilibrium from two different directions.

These tentative results indicate that niobium (in uranium-free solutions) should be soluble at room temperature when the F/Nb mole ratio exceeds 5.

### 6.2 Qualitative Tests of the Stability of the Uranium-Niobium Solutions

The purpose of these tests was to determine the conditions necessary for achieving stable $HNO_3$-HF and HF solutions containing uranium and niobium after having boiled the solutions. The initial work was conducted with freshly precipitated hydrous niobic oxide to ensure rapid dissolution of the samples.

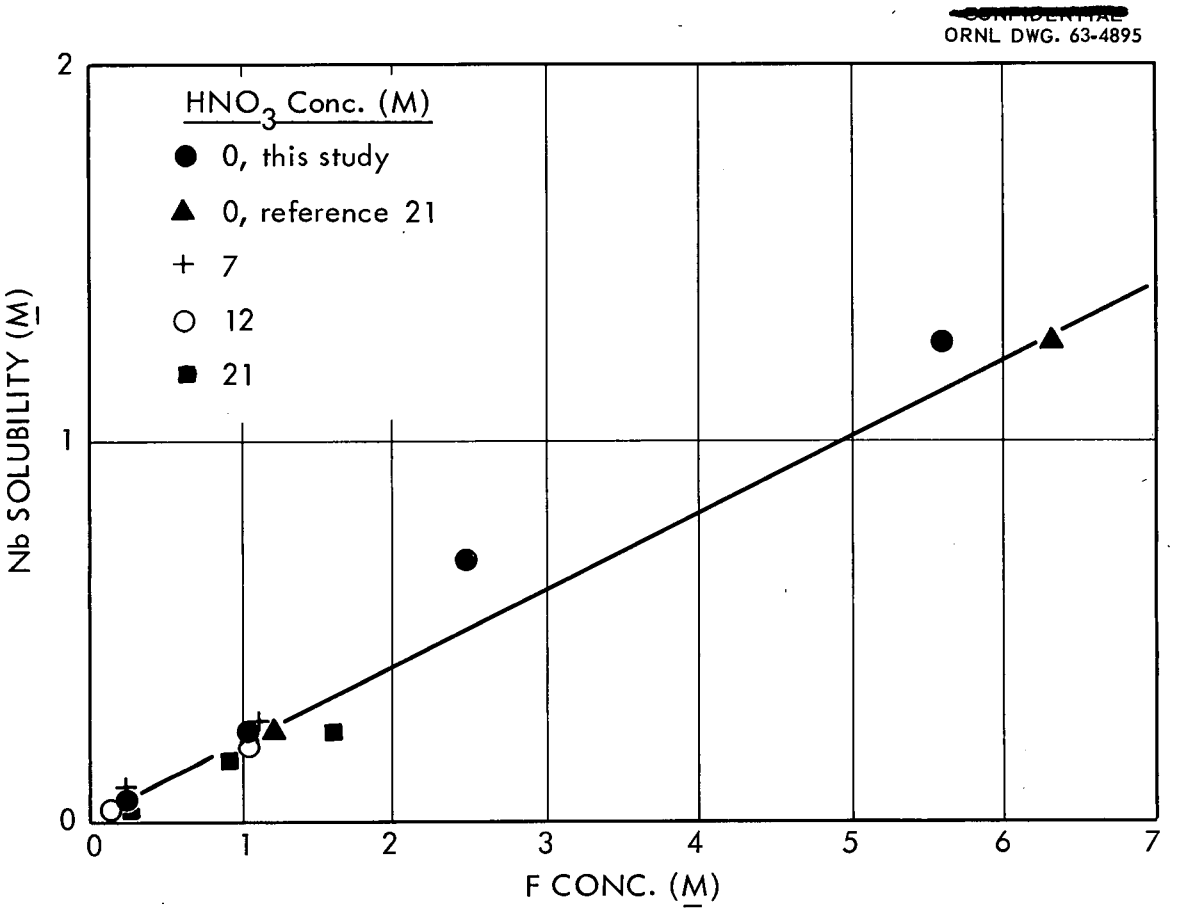


Fig. 8. Tentative Solubility Data for $Nb_2O_5$ in HF and HF-$HNO_3$ Solutions at 26°C. Line drawn such that the F/Nb mole ratio is 5.

Table 9. Preliminary Data on the Solubility of $Nb_2O_5$ in HF and HF-$HNO_3$ Solutions at 26°C

| Solution Composition (M) | | | | |
|---|---|---|---|---|
| Initial | | Final | | |
| $HNO_3$ | HF | $NO_3^-$ | $F^-$ | Niobium Solubility (M) |
| 0 | 0.25 | 0 | 0.24 | 0.053 |
| 0 | 1.0 | 0 | 1.06 | 0.237 |
| 0 | 2.5 | 0 | 2.45 | 0.693 |
| 0 | 5.0 | 0 | 5.58 | 1.25 |
| 0 | 10 | 0 | 10.6 | 2.34 |
| 0 | 15 | 0 | 14.3 | 3.23 |
| 7.5 | 0.25 | 7.56 | 0.25 | 0.046 |
| 7.5 | 1.0 | 7.24 | 1.10 | 0.232 |
| 12.5 | 0.25 | 12.4 | 0.20 | 0.031 |
| 12.5 | 1.0 | 12.5 | 1.03 | 0.204 |
| 21 | 0.25 | 21.3 | 0.20 | 0.030 |
| 21 | 1.0 | 20.6 | 0.92 | 0.173 |
| 21 | 2.0 | 19.7 | 1.56 | 0.243 |

The stability of solutions resulting from 16-hr dissolutions of the hydrous oxide in a variety of boiling $HNO_3$-HF solutions where the F/Nb mole ratio was 10 was affected mainly by the HF concentration. In general, solutions having an HF concentration greater than 0.5 M were stable on cooling to room temperature, irrespective of the nitric acid concentration,which was varied from 3 to 10 M (Fig. 9). Virtually all solutions having HF concentrations of 0.3 M or less yielded, on cooling, precipitates containing $NbO_2F \cdot 1/2\ H_2O$ and another, unidentified compound, possibly $NbOF_3$.

Stable solutions resulted from 5-hr dissolutions of niobium metal in either 2 M $HNO_3$--5 M HF or 5 M $HNO_3$--1 M HF when the F/Nb mole ratio was 10.

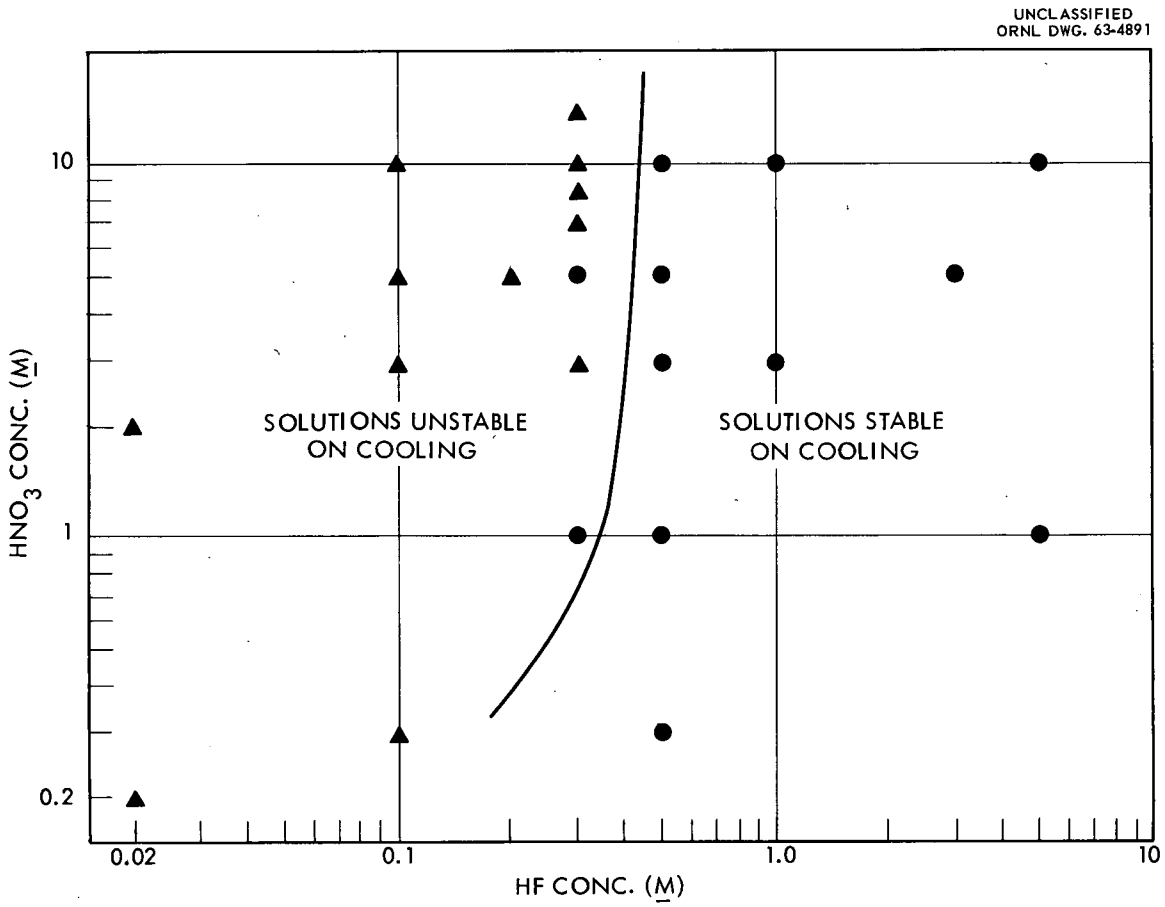


Fig. 9. Stability of $HNO_3$-HF Solutions Containing Niobium After Boiling for 18 hr and Cooling to Room Temperature. The F/Nb mole ratio was 10 in each case.

Similar results were obtained starting with NbC instead of the metal; the dissolution period in these experiments was 20 hr instead of 5.

No definitive solubility measurements have yet been made on systems containing both uranium and niobium. However, the preparation of stable solutions during Deline-Burn-Dissolve (Sec 2) and Burn-Dissolve (Sec. 3) experiments indicate that uranium should have little effect on the niobium solubility when the F/Nb mole ratio is 8 or higher.

## 7. STUDIES OF THE ELECTRODISINTEGRATION OF GRAPHITE-BASE FUELS

Graphite-base reactor fuels can be disintegrated by making them anodes in nitric acid solutions.[5,6,22,23] With fuels which did not contain coated particles, uranium was simultaneously dissolved by the acid. However, in tests with coated-particle fuel element samples, little uranium was recovered in the acid even though the graphite matrix was disintegrated.[6,23,24] These tests indicated that the carbon coatings were not destroyed by the anodic attack. Additional experiments were conducted with samples of carbon-coated particles (not dispersed in a graphite matrix) to confirm the prior findings.[23]

Two pieces of experimental equipment, a U-shaped "series" dissolver[25] and a direct-anode-contact dissolver,[22] were constructed for use in these experiments. In each series of experiments, the current density and the temperature were varied. The particles used in these experiments were 147- to 417-μ $UC_2$-$ThC_2$ particles coated with 55- to 60-μ of pyrolytic carbon by General Atomics. These particles contained 18.6% uranium and 43.3% thorium. To determine suitability for use in the electrodissolver tests, a sample of the particles was leached for 5 hr in boiling 90% $HNO_3$, another disintegration agent. Only 0.006% of the uranium and 0.025% of the thorium were leached by the acid, showing that the particle coatings were of high integrity.

Under all conditions used (current density, 1 to 10 amp/$cm^2$; $HNO_3$ concentration, 10 M; temperature, 25 to 80°C), more than 99.9% of both the uranium and

thorium was retained by the particles (Table 10). These experiments with coated particles support the results of prior studies[5,6,22-24] and indicate that electrodisintegration would result in little or no uranium recovery from Rover fuel elements that contained coated particles.

Table 10. Data from Electrolytic Dissolution Experiments with Carbon-Coated $UC_2$-$ThC_2$ Fuel Particles

Electrolyte: 10 M $HNO_3$
Contact time: 7 hr

| Type of Dissolver | Current Density ($amp/cm^2$) | Temp. (°C) | Amount Dissolved (%) | |
|---|---|---|---|---|
| | | | Uranium | Thorium |
| Direct Anode | 1 | 30 | 0.02 | 0.16 |
| Series | 0 | 25 | 0.01 | 0.01 |
| Series | 1 | 25 | 0.01 | 0.01 |
| Series | 1 | 37 | 0.1 | 0.1 |
| Series | 1 | 52 | 0.01 | 0.04 |
| Series | 1 | 80 | 0.01 | 0.01 |
| Series | 10 | 40 | 0.01 | 0.01 |

## 8. METALLIC-CORE ROVER FUEL

Recently, new interest has arisen on the use of metallic-core, unmoderated reactors for Rover application.[26] The fuel of primary interest is $UO_2$ dispersed in a tungsten matrix. This type of fuel was proposed at Los Alamos Scientific Laboratory several years ago for Dumbo reactors,[27] which were considered as alternatives to the graphite-base Kiwi reactors. Preliminary experiments were conducted at ORNL in 1959 on the processing of the Dumbo type of Rover fuel.[28] The experiments were based on the fact that similar fuels could be dissolved in nitric acid in the presence of ions ($PO_4^{3-}$ and $Fe^{3+}$) capable of forming soluble heteropolymolybdate and heteropolytungstate ions.[29]

Simulated $UO_2$-W fuels containing 25% $UO_2$ were dissolved in boiling 2 M $HNO_3$--1 M $H_3PO_4$, yielding solutions containing 0.13 M W and 0.03 M U (Fig. 10). The terminal hydrogen ion concentration, about 3.4 M, includes all the hydrogen ion from the nitric acid and the hydrogen ion from the dissociation: $H_3PO_4 \longrightarrow H^+ + H_2PO_4^{2-}$. Because samples of prototype fuel were not available, the experiments were conducted by using the appropriate quantities of 3-mil-thick tungsten sheet and $UO_2$ pellets. Complete dissolution of both the tungsten and $UO_2$ required about 10 hr.

Preliminary attempts to dissolve tungsten in boiling 5 M NaOH prior to dissolution of the $UO_2$ in nitric acid were unsuccessful. Tungsten could not be dissolved in boiling 2 M $HNO_3$--1 M $Fe(NO_3)_3$, a good dissolvent for molybdenum and U-Mo alloys.[29] Further experiments on the processing of $UO_2$-W cermet fuels will be conducted when fuel samples become available.

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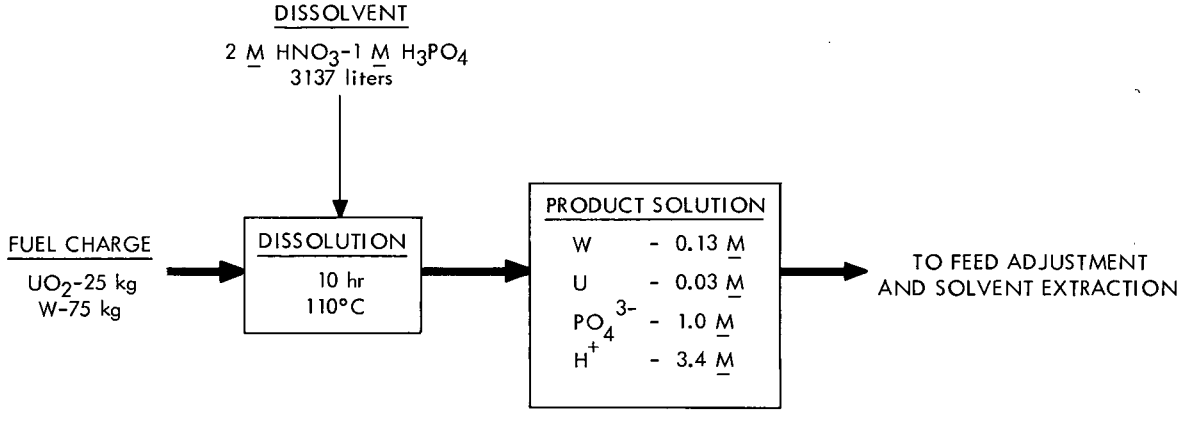


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# APPENDIX A

## TEFLON APPARATUS FOR USE WITH BOILING HF-$HNO_3$ SOLUTIONS

Because of the wide interest in laboratory equipment for handling boiling solutions of high hydrofluoric acid concentration, the apparatus used here will be described.

The reaction vessels (Fig. A.1) were machined from commercial 3-in.-OD, 6-in.-long "100% Prime Virgin Teflon" rod. The final dimensions of the cylindrical cavity were 57 mm in diameter and 148 mm in length. The outside surface of the rod was turned down on a lathe to a diameter of 63 mm leaving a 6-mm flange at the open end.

The condenser core consisted of commercial Teflon tubing (1-in.-OD, 5/8-in.-ID, and 24 in. long), which was turned down to about 22 mm OD to obtain a thinner wall to increase heat transfer. One end was threaded to receive (1) a Teflon locknut and (2) a Teflon flanged disk, drilled and threaded, which served as the cover for the reaction vessel. The condenser jacket was fabricated from 48-mm Pyrex tubing, closing the ends with rubber stoppers which had been suitably bored to receive the Teflon condenser core. The locknut and flanged disk were not removed from the condenser except for special cleaning.

Assembly of the equipment (Fig. A.1) was accomplished by fitting the mating surface of the flanged disk to the flange of the reaction vessel, and attaching three or four metal clamps which had been enamelled to prevent their corrosion. With the clamps in position, the seal was virtually gas tight. Standard heating mantels were employed, with the addition of a double layer of heavy, aluminum foil between the bottom of the Teflon dissolver and mantel surfaces to distribute the heat uniformly about the lower end of the Teflon vessel.

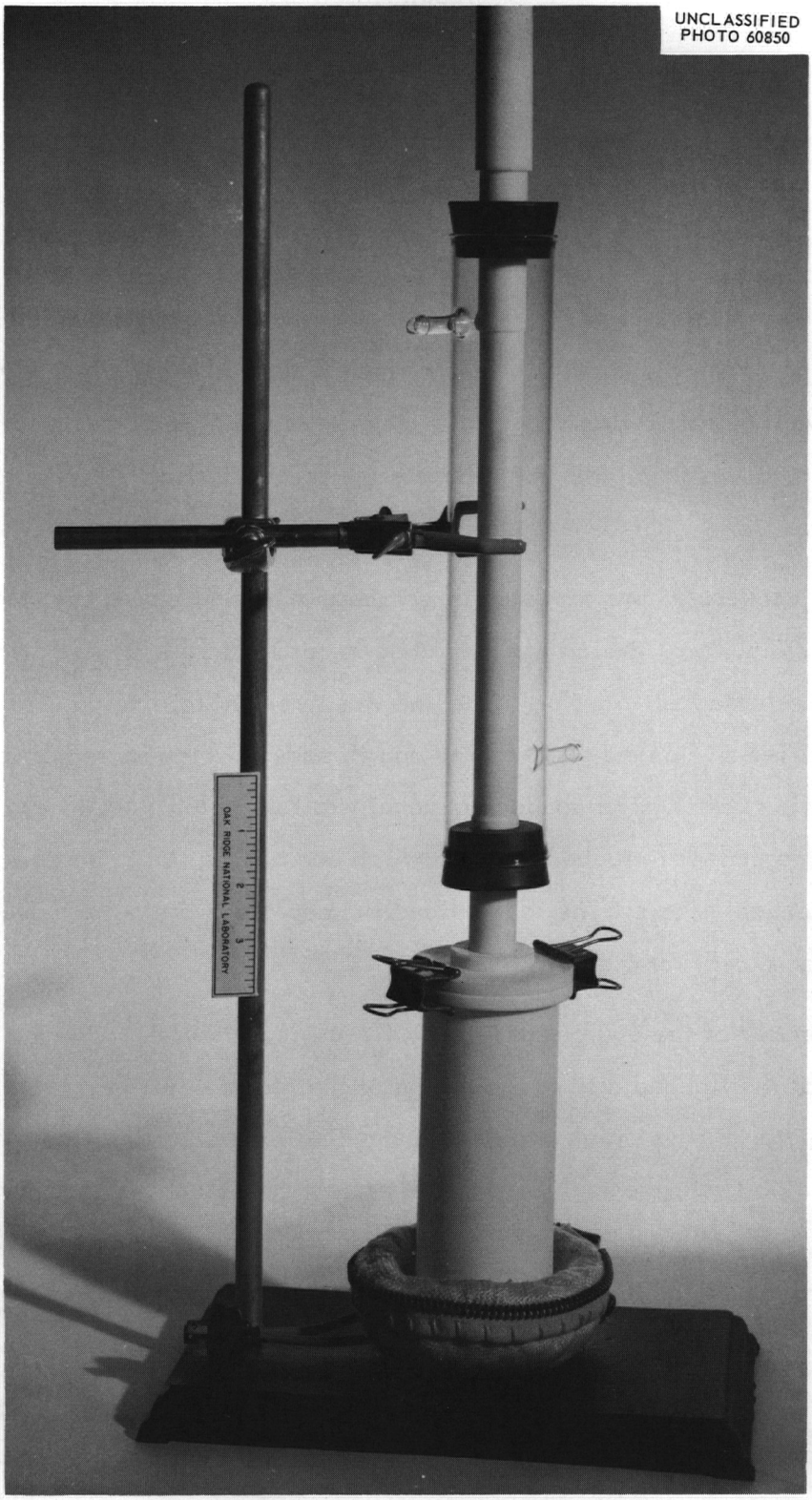


Fig. A.1. Teflon Apparatus for Containing Boiling HF and HF-$HNO_3$ Solutions.

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