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## ROVER REPORT FOR FEBRUARY 1963

F. L. Culler, Jr.

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CONTENTS

Page

Abstract . . . . . 4

1. Introduction . . . . . 5

1.1 Brief Survey of the Problem and the Research . . . . . 5

1.2 Status and Evaluation of the Efforts . . . . . 7

2. Recovery of Uranium from Spent Rover Fuel by the Combustion-Fluorination Process . . . . . 8

2.1 Introduction . . . . . 8

2.2 Status of Development . . . . . 9

2.3 Current Work . . . . . 9

2.3.1 Combustion . . . . . 9

2.3.2 Fluorination . . . . . 18

2.3.3 Breaking Tests on Prototype Fuel . . . . . 18

2.4 Conclusions . . . . . 19

3. Aqueous Process for Recovering Uranium from Rover Fuel Combustion Ash . . . . . 22

3.1 Development of the Deline-Burn-Dissolve (DBD) Flowsheet . . 22

3.1.1 Delining Studies . . . . . 22

3.1.2 Preliminary Flowsheet . . . . . 22

3.1.3 Experiments Based on the Flowsheets . . . . . 25

3.2 Development of the Burn-Leach Process . . . . . 25

3.3 Combustion of Irradiated Rover Fuel . . . . . 27

4. Chlorination and Chloride Volatility Studies on the Recovery of Uranium from Rover Fuel Combustion Ash . . . . . 28

4.1 Combustion-Hexachloropropene-Chlorination Process . . . . . 28

4.2 Corrosion Tests Relating to Chlorination with Hexachloropropene . . . . . 32

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## ABSTRACT

Laboratory-scale and engineering-scale efforts to recover uranium (and possibly the niobium) from spent Rover fuel elements are reported, and the status of each aspect of the work is presented, including the evaluations.

Basically, the fuel consists of pyrolytic-carbon-coated spheroids of uranium carbide dispersed in a graphite matrix. The coolant channels in the graphite are lined with niobium carbide. For uranium recovery, in essence the fuel element is first oxidized to remove the graphite, leaving an ash that contains principally the oxides of uranium and niobium; then, the uranium will be separated from the niobium and nonvolatile fission products by appropriate methods. Most of the chemical problems are associated with the niobium and the pyrolytic carbon coating.

The Combustion-Fluorination Process represents the main effort, and basically it involves the combustion of the fuel and the fluorination of the ash; the uranium is recovered as $UF_6$. The method is in the pilot-plant stage of development. This issue includes the following information: the procedure, results, and evaluation of a 14,162-g combustion run in the 5-in.-diam reactor, the material balance (uranium) for the first fluorination run, and the results of tests on the breaking of fuel rods prior to their being charged to the reactor.

Alternatives to combustion-fluorination involve the dissolution of the ash with hydrofluoric-nitric acid mixtures, thereby preparing solutions adaptable to the solvent-extraction separation of the niobium, uranium, and fission products. Several processes are based on this system, and they are: the Deline-Burn-Dissolve, the Burn-Dissolve, and the Burn-Leach Process. Reported in this issue is a tentative flowsheet for the Deline-Burn-Dissolve Process. These methods are in the laboratory stage, though some pilot-plant work has been done on the Deline-Burn-Dissolve method.

Other alternatives to combustion-fluorination include the gaseous chlorination of the combustion ash to form the volatile, separable chlorides of niobium and uranium, and the chlorination of the ash with hot hexachloropropene (HCP) followed by appropriate solvent extraction steps to separate

the niobium and uranium. These methods are in the laboratory stage of development. Reported in this issue is a recently developed flowsheet for the HCP approach.

Supporting work is also reported.

## 1. INTRODUCTION

### 1.1 Brief Survey of the Problem and the Research

The studies are being made in order to develop an efficient and economical process for the recovery of uranium from spent Rover fuel, which consists of uranium carbide (coated with pyrolytic carbon) dispersed in graphite, with niobium carbide liners in the coolant channels. The burnup of the elements will be low, and they will not be excessively radioactive. The problems derive principally from the pyrolytic-carbon coating on the uranium carbide spheres and from the niobium carbide liners for the coolant channels.

The coating is very resistant to chemical attack, and a preliminary step in the process necessarily is the removal of the coating, whether or not this step is to be followed by fluorination, chlorination, or aqueous processing. This first step is conveniently done by simple combustion, which also includes the advantage of removing the bulk of the fuel element (the graphite moderator) as carbon dioxide. Then, the ash (oxides of uranium, niobium, and nonvolatile fission products) may be fluorinated, chlorinated, or treated by an aqueous mixture of hydrofluoric and nitric acids in order to recover the uranium. It may even be possible to eliminate hydrofluoric acid, according to a recently introduced variant of the aqueous-processing route. The combustion step, on the other hand, may or may not result in sintered oxides of uranium and niobium, depending on the controllability of the temperature, and dense sinters may make other steps in the recovery more difficult to take. As stated above, the niobium carbide liners and the pyrolytic-carbon coatings on the fuel spheres are presenting the most difficult problems and consequently requiring the most attention, whatever the approach.

The main effort is the Combustion-Fluorination Process, which essentially consists in burning the element in oxygen in order to produce a combustion ash, and then fluorinating the ash in order to separate the uranium (as the volatile hexafluoride) from the fluorides of niobium and the fission products. Some of the fission products are also volatile, as is niobium fluoride, but, due to their physical properties, they can be separated from the uranium by adsorption on beds of sodium fluoride, for example. The Combustion-Fluorination Process is in the pilot-plant stage of development.

The alternative methods for recovering the uranium from the combustion ash are the aqueous nitric-hydrofluoric acid process and the liquid- or gas-phase chlorination processes and their variants. According to the aqueous route, it may be possible to circumvent the sintering of the niobium pentoxide by first dissolving the liners from the elements in order to prevent the appearance of niobium oxide in the combustion ash, thereby improving the process whether the postcombustion steps follow an aqueous or a gaseous route. That development is called the Deline-Burn-Dissolve (DBD) Process and has advanced to the point of a pilot-plant study. Two variations of the DBD Process have also been introduced: the Burn-Dissolve and the Burn-Leach Processes. The Burn-Leach Process, should it be workable, offers the advantage of eliminating hydrofluoric acid from the aqueous processing.

The other alternative to the Combustion-Fluorination Process is one that basically involves the liquid-phase, low-temperature chlorination of the combustion ash with hexachloropropene (HCP), or high-temperature, gas-phase chlorination, plus the useful variants that may develop as the study advances. Liquid- or gas-phase chlorination have so far shown themselves worthy of study because early corrosion results indicate that the nickel reactor will not be attacked severely. Gas-phase chlorination is very similar in many important respects to the fluorination method, but liquid-phase chlorination with HCP has special advantages. For example, it is run at low temperature (below 200°C), and the product is readily adaptable to extraction by tributyl phosphate--Amsco mixtures. On the other hand, gas-phase chlorination may offer promise as a method not only

for separating the uranium in bulk but for purifying it, though this has yet to be demonstrated. The gas-phase work is done in an apparatus called the "Torrefactor."

Laboratory work in support of the processes is continuing to help identify and solve problems as they arise.

The status and evaluation section below is confined to the progress made on the work done during this reporting period. The other progress reports in this series are: ORNL-TM-170, 199, 227, 267, 298, 373, 408, 426, 443, and 509.

## 1.2 Status and Evaluation of the Efforts

Recovery of Uranium from Spent Rover Fuel by the Combustion-Fluorination Process. The predicted 8 hr for burning one batch of fuel in the 5-in.-diam reactor will probably cover charging and preheating time. Two successive batches could be oxidized in 18 hr, and the combined oxides (combustion ash) could be fluorinated in the remaining 6 hr to provide a capacity of about 5 kg of uranium per 24 hr per 5-in.-diam reactor.

The fluorination and separation operations still need further study; however, a high recovery and a clean separation seem possible.

The use of broken fuel as a reactor charge is practical. The results of breaking unirradiated coated-particle fuel indicate that aqueous delining of the fuel elements might be used for removing the niobium carbide liners from the elements. In other words, coated fuel particles may not be ruptured, exposing the uranium carbide to the delining solution, which can leach the uranium.

Development of the Deline-Burn-Dissolve Flowsheet. The key factors of the process were tested with uncoated fuel, and the method seems to be useful. When pyrolytic-carbon-coated fuel becomes available, the process will be tested with both irradiated and unirradiated fuel. That should conclude the laboratory phase of the study, except for an intensive investigation of the corrodibility of the stainless-steel containers used in the delining and burning steps, and of the corrodibility of the solvent extraction equipment.

Combustion-Hexachloropropene-Chlorination Process. A process was developed in the laboratory for the chlorination of combustion ash with hot, liquid hexachloropropene (HCP), followed by the extraction of the product chlorides from the HCP with water. The uranium is then extracted from that aqueous solution with a tributyl phosphate--Amsco mixture.

The process appears to be adaptable to large-scale work because all the operations involve the handling of solutions only. Uranium losses to the HCP were only 0.001%, and to the raffinate, less than 0.02%.

Unsolved problems are: the effect of niobia on the operation of a countercurrent extraction column, and the effect of chloride on the extraction columns and on the extraction efficiency.

Corrosion Tests Relating to Chlorination with Hexachloropropene. The corrosion rate for type 304L stainless steel in a refluxing bath of hexachloropropene, with and without dissolved $U_3O_8$, was less than 0.4 mil/month for a 24-hr exposure. It was (overall) 0.12 mil/month for 264 hr of exposure. Other metals were corroded to about the same small extent, indicating that the choice of a container material for hot hexachloropropene or hot hexachloropropene-uranium chloride solution will be an easy one.

## 2. RECOVERY OF URANIUM FROM SPENT ROVER FUEL BY THE COMBUSTION-FLUORINATION PROCESS

R. W. Horton
R. S. Lowrie
F. G. Kitts
L. E. McNeese

### 2.1 Introduction

The fuel being used in reactors designed for the Rover project is a dispersion of enriched uranium carbide in graphite, and the large amount of uranium required for ground testing justifies uranium recovery. The use of pyrolytic-carbon protective coatings on the uranium particles, and the use of niobium carbide liners for the propellant-gas passages makes the chemical separation of uranium from graphite very difficult when using conventional aqueous methods. Hence, new process methods designed expecially for this fuel are being developed. At present, the

most feasible methods all use combustion with oxygen to eliminate the graphite and the fuel coating and to convert the uranium and niobium carbides to oxides. The separation of uranium from other combustion products by an aqueous method (Deline-Burn-Dissolve Process) and by the fluoride volatility process is being studied on a pilot-plant scale.

## 2.2 Status of Development

A large-scale test apparatus for the development of the combustion and fluorination process for Rover fuel was constructed. The unit presently includes a 5-in.-diam cylindrical reactor for combustion and fluorination of 2- to 3-kg batches of uranium, a distillation column, and sodium fluoride sorption beds for product separation. A slab-type reactor vessel having a capacity of 5 to 6 kg of uranium per batch is being built in the ORNL shops for use in this system.

Two oxidation test runs were made, and the oxide from the first run was fluorinated. The oxidation rate in the second test was about twice that of the first run (about 8 hr total combustion time, vs 15 hr). The oxides were slightly slagged in the second run but are not expected to require significantly longer fluorination time.

The second run was made with the fuel rods broken into right cylinders. The charge capacity was reduced from 58 to 50 rods (27-in. rods), but this had no effect on the oxidation of the fuel elements. The amount of fines produced was about 1%. In a breaking test of 19-hole coated-particle fuel, breaking the rods into 3/4-in. lengths resulted in the rupture of about 0.3% of the fuel particles.

## 2.3 Current Work

### 2.3.1 Combustion

Combustion run 0-2 was made with a charge of fifty 27-in. rods (as noted above) broken into approximate right cylinders, which were dumped into the reactor. The charge weighed 14,162 g. The charge was pre-ashed to a 5.1% burnup, with a low air rate during the heat-up period, and then

burned with oxygen in 5 hr. An additional 1-hr burning period was used to test the completeness of burning; during this hour, about 2 g-moles of carbon was burned (calculated from chromatographic data). Overall oxygen utilization for the run was 55%, and 4500 g of oxide was produced. The ash had a bulk density of 2.4 g/cc and included some fused pieces as large as 2 x 2 x 0.5 in. These pieces were very irregular, quite friable, and showed internal porosity when broken. Previous experience with this type of material indicates that it should fluorinate readily.

The procedure for this run was based on a set of arbitrary conditions. They specified that: (1) minimum burning time (maximum rate) consistent with acceptable temperatures was the prime objective; (2) the simplest possible method of oxidizing-gas feed control would be used; and (3) if excessive amounts of carbon monoxide were generated, dilution with inert gas above the fuel bed would be the only control.

Accordingly, the procedure meeting these requirements called for an air-oxygen mixture that contained 50% oxygen to be fed to the bottom zone of the reactor, and oxygen to be added to each of the four upper zones in a quantity sufficient to restore the total gas composition to 50% oxygen at each entry point. (In calculating the oxygen requirement of the upper zones, it was assumed that all oxygen fed below each point had been converted to $CO_2$). With these flow ratios established by appropriate settings of the individual zone rotameters, the total quantity fed could be controlled by use of one master valve and flowmeter. A nitrogen supply was connected to the top purge line of the reactor, and it enters about 6 in. above the top of the fuel bed (as charged). This supply was to be used for carbon monoxide dilution when required. Thermocouples (Pt vs Pt-Rh) in nickel sheaths were located at the center line of the bed at each gas-entry level. A maximum reading of 1350°C at any zone was set as the rate-limiting point.

The procedure also specified that the fuel would be pre-ashed to 5% burnup by admission of air to the bottom zone only during the reactor heating-up period. All calculations of burning rate, percentage of burnup and oxygen utilization were to be based on chromatographic analysis of the off-gas and on the measured input gas flow. Carbon monoxide

readings were to be taken continuously from a combustion cell and intermittently from the chromatograph.

The procedure was followed in the actual run, with some exceptions. The more important of these were: (1) the air flow to the bottom zone was stopped fairly early in the run; (2) during the last portion of the run, the oxygen flow to the upper zones was stopped because the centerline temperatures indicated that the remaining fuel bed had slumped below these zones; and (3) no diluent nitrogen was used for carbon monoxide control due to nonagreement between the continuous-reading combustion cell and the intermittent indication from the gas chromatograph. The carbon monoxide content was in the range of 5 to 15% for about 15 min; the high value came from chromatograph samples that are read every 5 min. At the end of this period, the carbon monoxide indication by both instruments fell off rapidly to 0%. During the period, the actual carbon monoxide concentration probably exceeded 10% for less than 10 min. It is probable that the use of air at all zones during the pre-ashing period would eliminate the carbon monoxide problem.

A plot of burning rate, oxygen utilization, and oxygen feed is shown in Fig. 1. The quantity of oxygen fed to each zone is indicated by the bar segments. It is interesting to note that when the total oxygen flow was routed to the three bottom zones at 1600 hr, a great increase in burning rate was noted. This apparently verifies the assumption that the fuel bed had slumped below the top zones prior to this time.

The centerline temperatures indicated by the thermocouples rose to peaks above 1350°C on a few occasions, but immediately fell back. The trace of all temperature points was cyclic, probably indicating the periods when the burning zone was in the vicinity of the thermocouple. The sheaths of the bottom three couples had been melted or oxidized and consequently had lost part of their length--the bottom-zone couple was 0.75 in. long at the end of the run. In spite of this damage, all thermocouples operated throughout the run. It is possible that molten oxides served as a flux to liquefy the nickel sheath at temperatures below the melting point (about 1440°C).

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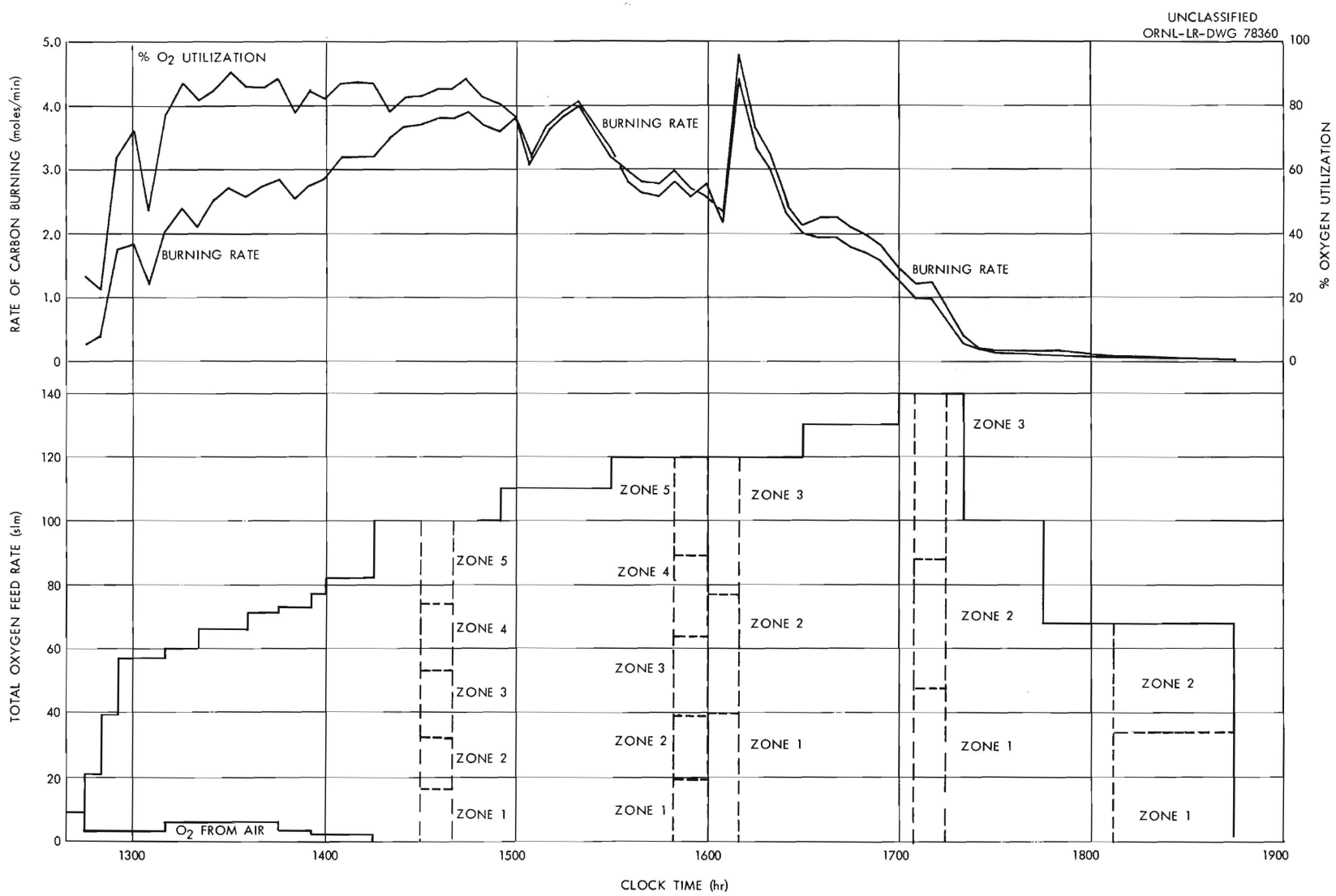


Fig. 1. Distribution and Utilization of Oxygen, and Burning Rate of Carbon for Run O-2.

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The reactor-wall temperatures were controlled by the use of air-water mixtures in the cooling coils wrapped around the reactor (Fig. 2). In this run, it was planned to hold the wall temperatures in the 400 to 500°C range. This amount of cooling was well below the maximum capacity of the system; however, it was noted that wall temperatures were subject to sudden and severe temperature excursions. These sudden rises in temperature were attributed to slumping of the broken-rod fuel bed, which allowed burning fuel to contact the walls randomly. In all cases it was possible to bring the temperature back into the control range by varying the amount of water supplied. A plot of one of these excursions is shown in Fig. 3, and the temperature points plotted are identified in Fig. 2.

A new gas-cooler and filter unit was tested in this run. The cooling unit is water-cooled and finned and is centrally located in the reactor, just above the fuel bed. The filters are external to the reactor in parallel 4-in. chambers. Each filter is a Rigimesh element, 3.5-in.-diam by 18-in. long, made of nickel wire. Thermocouples were attached to the bottom and top of the finned cooling unit, and also inserted in the gas stream going to the filters. The maximum recorded temperatures at these locations were 270, 100, and 75°C, respectively.

Only one of the two parallel filter units was in service during the run, although the valving was arranged to allow change-over and/or blowback without shutdown. A small pressure buildup across the filter, about 15%, resulted from the entire operation. The filter was examined at the end of the run and was found to be covered with a thin film of fine solids. These were easily brushed off; they weighed 13.5 g. There was evidence of fine-particle accumulation downstream from the filters in such locations as the chromatograph sample-line rotameters.

Samples were taken at the end of the run and submitted for chemical analysis. These results are shown in Table 1. The general appearance of the ash (metal oxide from fuel) is shown in Fig. 4 and 5.

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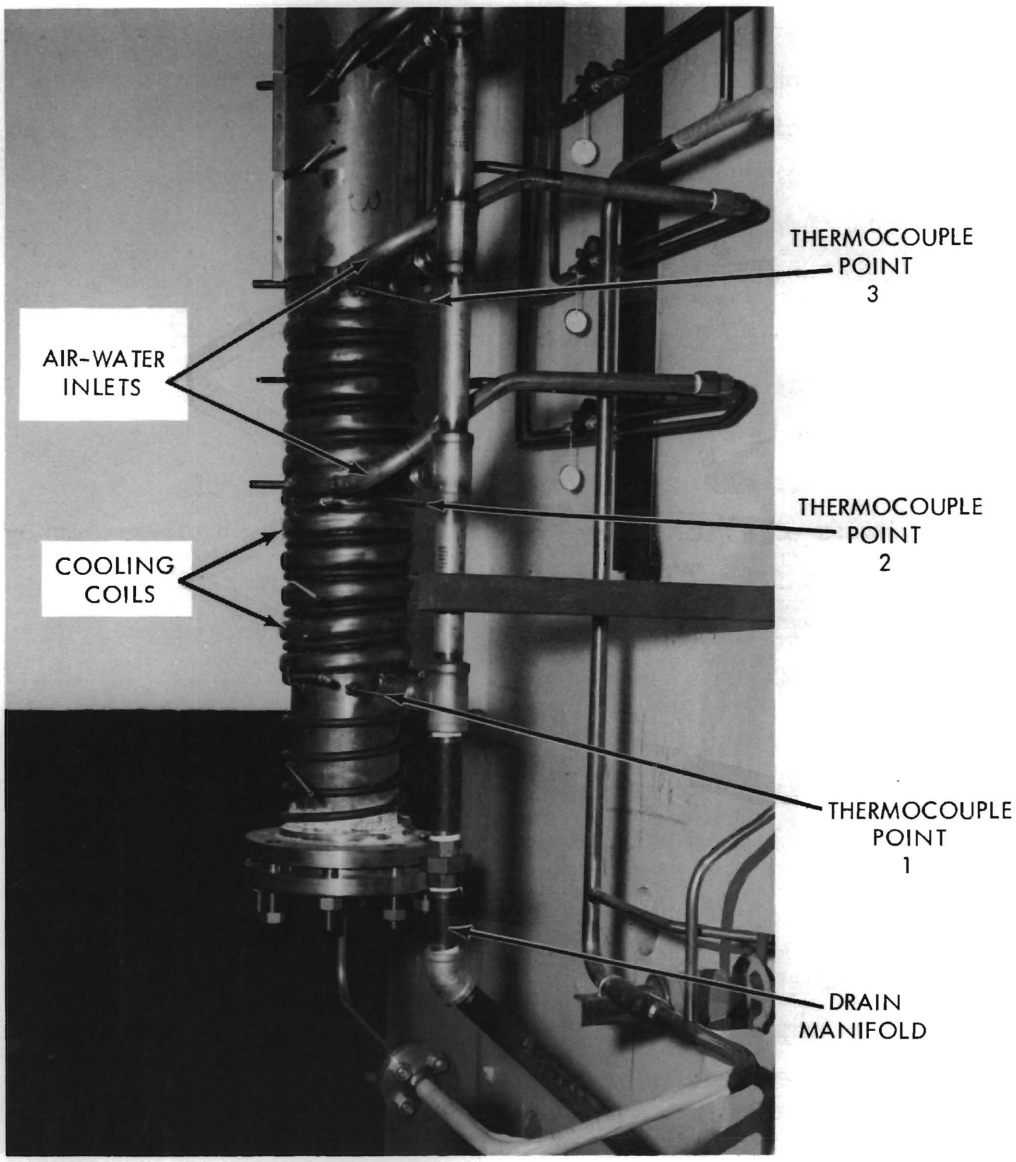


Fig. 2. Five-inch-Diameter Reactor: Cooling System and Location of Thermocouples.

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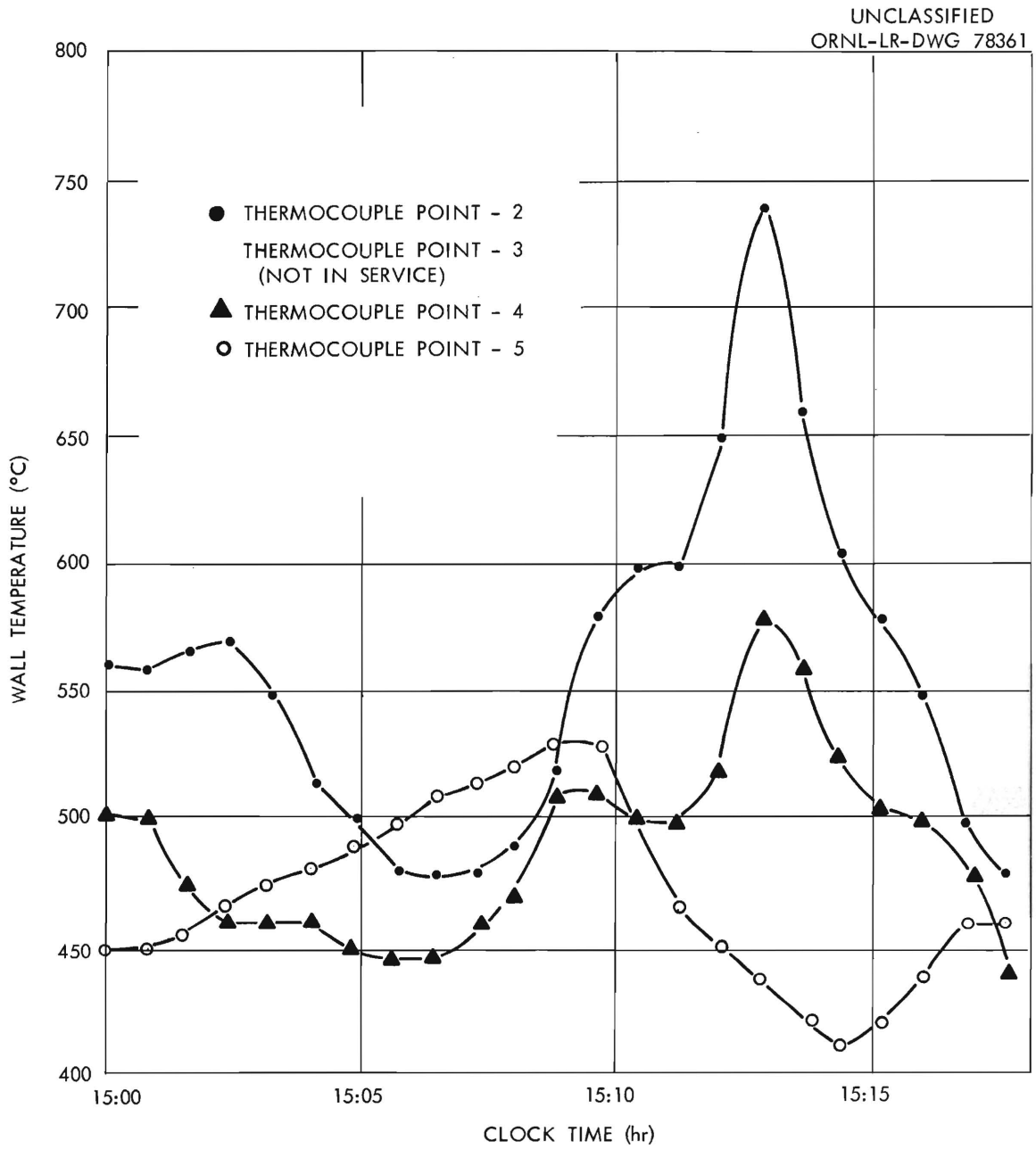


Fig. 3. Maximum Excursions of Wall Temperature.

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Fig. 4. Oxides from Combustion Run O-2.

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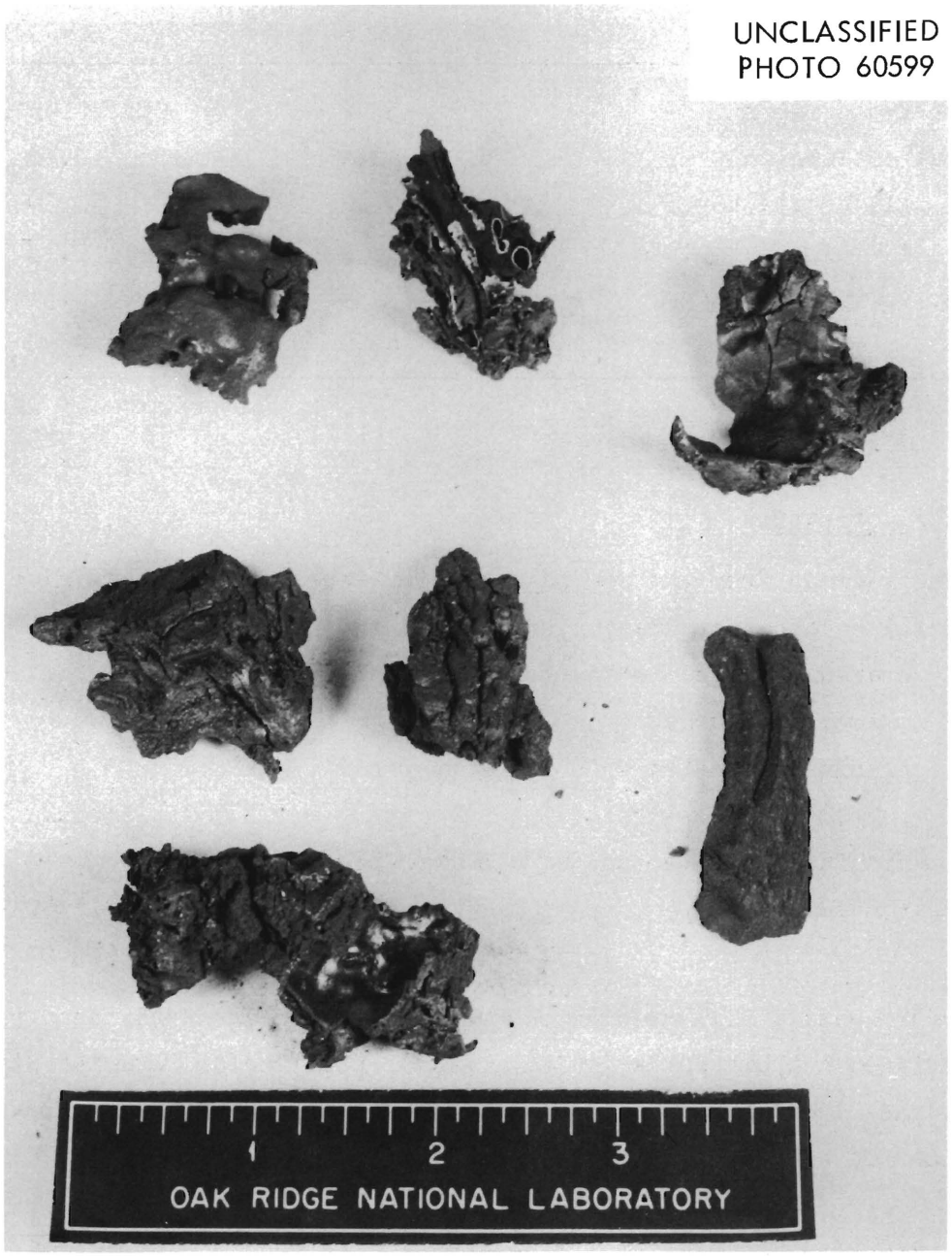


Fig. 5. Selected Specimens of Oxides from Combustion Run O-2.

[redacted]

Table 1. Analysis of Reactor Residues, Run 0-2

| Description of Samples | Total Wt (g) | U (%) | Nb[a] (%) | Ni (%) | Fe (%) | Carbon (%) |
|---|---|---|---|---|---|---|
| Residue from filter | 13.5 | 33.7 | | 0.18 | 0.45 | |
| Internal cooling unit | 5 | 40.4 | | 0.56 | 0.46 | |
| Inside wall of reactor | 29 | 16.2 | | 3.50 | 0.59 | |
| Ash No. 1, thin flat plate | 4500 | 25.5 | | 0.44 | 0.33 | 0.005 |
| Ash No. 2, fines | | 37.4 | | 0.23 | 0.34 | 0.01 |
| Ash No. 3, massive sinter | | 43.0 | | 0.09 | 0.30 | 0.005 |

[a]Figures not available.

### 2.3.2 Fluorination

The residue from the second oxidation tests has not been fluorinated. A material balance for uranium on run F-1 shows:

| | | |
|---|---|---|
| Uranium charged to reactor (calculated from SS record), g | 2,575.0 | |
| Uranium collected on NaF absorber bed V-104, g | | 85.29 |
| Uranium collected on NaF absorber bed V-105, g | | 2,515.80 |
| Total weight, g | | 2,601.09 |

This represents a 101% uranium recovery. The niobium analyses are not yet verified but presently indicate almost no transfer from the still to the sodium fluoride beds. This recovery and separation was achieved during fluorination without a subsequent distillation step.

### 2.3.3 Breaking Tests on Prototype Fuel

Breaking tests on 19-hole hexagonal fuel rods containing pyrolytic-carbon-coated $UC_2$ particles resulted in the fracturing of less than 0.3% of the coated particles, as determined by leaching[1] the dust and the 3/4-in.

[1]F. L. Culler, Rover Report for December 1962-January 1963, ORNL-TM-509.

broken lengths (Table 2). Leaching consisted in an 8-hr contact with 15.8 M $HNO_3$ at 95 to 100°C. Other data from the breaking tests, for example, energy requirements and amount of fines produced, were also reported in the December-January Rover report.[1] Data taken while breaking a 50-rod batch of lined fuel showed that the amount of fines produced was about 1%. The higher yield of fines was expected because of the presence of liner material. However, the increase was not entirely due to the liner contribution: a number of rods were cracked to varying degrees (Table 3). The fluted rods produced more fines and slivers than the cylindrical rods.

Examination of the 30° blade used to break the 50-rod batch disclosed some upsetting of the cutting edge, apparently due to the action of the NbC liner on the relatively soft blade (mild steel, hardened to 84 to 90 Rockwell B). There was no indication of any change in breaking characteristics, and, in any case, substitution of a hardened machine-steel blade or metal carbide insert will probably give adequate service.

## 2.4 Conclusions

1. The predicted 8 hr for burning one batch of fuel in the 5-in.-diam reactor will probably cover charging and preheating time. Two successive batches could be oxidized in 18 hr, and the combined oxides could be fluorinated in the remaining 6 hr to provide a capacity of about 5 kg of uranium per 24 hr per 5-in. reactor.

2. The fluorination and separation operations still need further study; however, a high recovery and a clean separation seem possible.

3. The use of broken fuel as a reactor charge is practical. The results of breaking unirradiated coated-particle fuel indicate that aqueous delining of the fuel elements might be used for removing the niobium carbide liners from the elements. That is to say, coated fuel particles may not be ruptured, exposing the uranium carbide to the delining solution, which can leach the uranium.

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Table 2. Guillotine Breaking of 19-hole Hexagonal Fuel (Unlined) Containing Pyrolytic-Carbon-Coated $UC_2$ Particles

Lengths of about 3/4 in., produced by the 30° blade with kinetic energy of 16 to 40 in.-lb

| | Test Number | | | | |
|---|---|---|---|---|---|
| | 6 | 7 | 8 | 17 | 19 |
| Weight of fines,[a] g | 0.024 | 0.022 | 0.016 | 0.016 | 0.011 |
| Total U, g | 0.0020 | 0.0018 | 0.0014 | 0.0029 | 0.0010 |
| Leachable U,[b] g | 0.00041 | 0.00038 | 0.00031 | 0.00051 | 0.00025 |
| Weight of pieces, g | ~10.4 | ~10.4 | ~10.4 | ~10.4 | ~10.4 |
| Total U, g | 0.844 | 0.836 | 0.839 | 1.74 | 1.74 |
| Leachable U,[b] g | 0.0022 | 0.0022 | 0.0005 | 0.0033 | 0.0031 |
| Total U, g | 0.846 | 0.838 | 0.840 | 1.743 | 1.74 |
| Total leachable U, g | 0.0026 | 0.0026 | 0.0008 | 0.0038 | 0.0032 |
| Percentage | 0.31 | 0.31 | 0.10 | 0.22 | 0.18 |

[a]Average from three breaks.

[b]Leached 8 hr in 15.8 M $HNO_3$ at 95 to 100°C.

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Table 3. Summary of Data Taken During Breaking a 50-Rod Batch of Fueled, Lined, Cylindrical Fuel Elements into 3/4-in. Lengths

| Batch Number | Number of Rods | Blade Clearance (in.) | Blade Kinetic Energy (in.-lb) | Wt of Pieces (g) | Wt of Fines (g) | Fines Produced (%) | Remarks |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 1/4 | 12-25 | 272 | 1.91 | 0.7 | |
| 2 | 1 | 1/4 | 12-25 | 195 | 23.0 | 11.7 | Badly broken, fluted rod |
| 3 | 3 | 1/4 | 12-40 | 871 | 8.40 | 0.96 | |
| 4 | 5 | 1/4 | 20 | 1318 | 28.5 | 2.16 | One fluted rod<br>One cracked rod |
| 5 | 10 | 1/4 | 20 | 2863 | 22.1 | 0.77 | |
| 6 | 10 | 1/4 | 20 | 2869 | 23.3 | 0.81 | One fluted rod<br>One cracked rod |
| 7 | 10 | 3/8 | 20 | 2797 | 26.8 | 0.96 | One cracked rod |
| 8 | 10 | 3/8 | 20 | 2814 | 30.3 | 1.07 | One fluted rod<br>One cracked rod |
| | 50 | | | ~14 kg | 164 g | ~1.2% | |

# 3. AQUEOUS PROCESSES FOR RECOVERING URANIUM FROM ROVER FUEL COMBUSTION ASH

L. M. Ferris K. S. Warren

## 3.1 Development of the Deline-Burn-Dissolve (DBD) Flowsheet

### 3.1.1 Delining Studies

The studies involving dissolution of NbC liners in nitric-hydrofluoric acid solutions were completed. Correlation of the data showed that delining is best accomplished when the hydrofluoric and nitric acid concentrations of the solution are greater than 1 and 3 M, respectively (Fig. 6). The delining can be initiated at room temperature with an F/Nb mole ratio of only 8, with results comparable to those obtained with boiling solutions. These experiments were conducted with Kiwi-B1A and -B2A specimens, which did not contain coated particles of uranium carbide. Consequently, it is probable that a few additional experiments will be required to ensure that actual coated-particle elements behave similarly. These tests will be started as soon as coated-particle fuel samples are available.

### 3.1.2 Preliminary Flowsheet

A tentative flowsheet (Fig. 7) has been evolved (ORNL-CF-63-1-75), and it is based on the delining data given above and on the following assumptions:

1. The fuel composition will be 15% uranium, 10% niobium, and 75% carbon.

2. Uranium will migrate from the coated particles into the NbC liner. For the sake of this argument, it was assumed that 10% of the uranium will be dissolved during the delining operation.

3. The delining solution and the solution obtained by nitric acid dissolution of the $U_3O_8$ combustion ash will be blended before solvent extraction.

4. The F/Nb mole ratio in the delining operation will be 8.

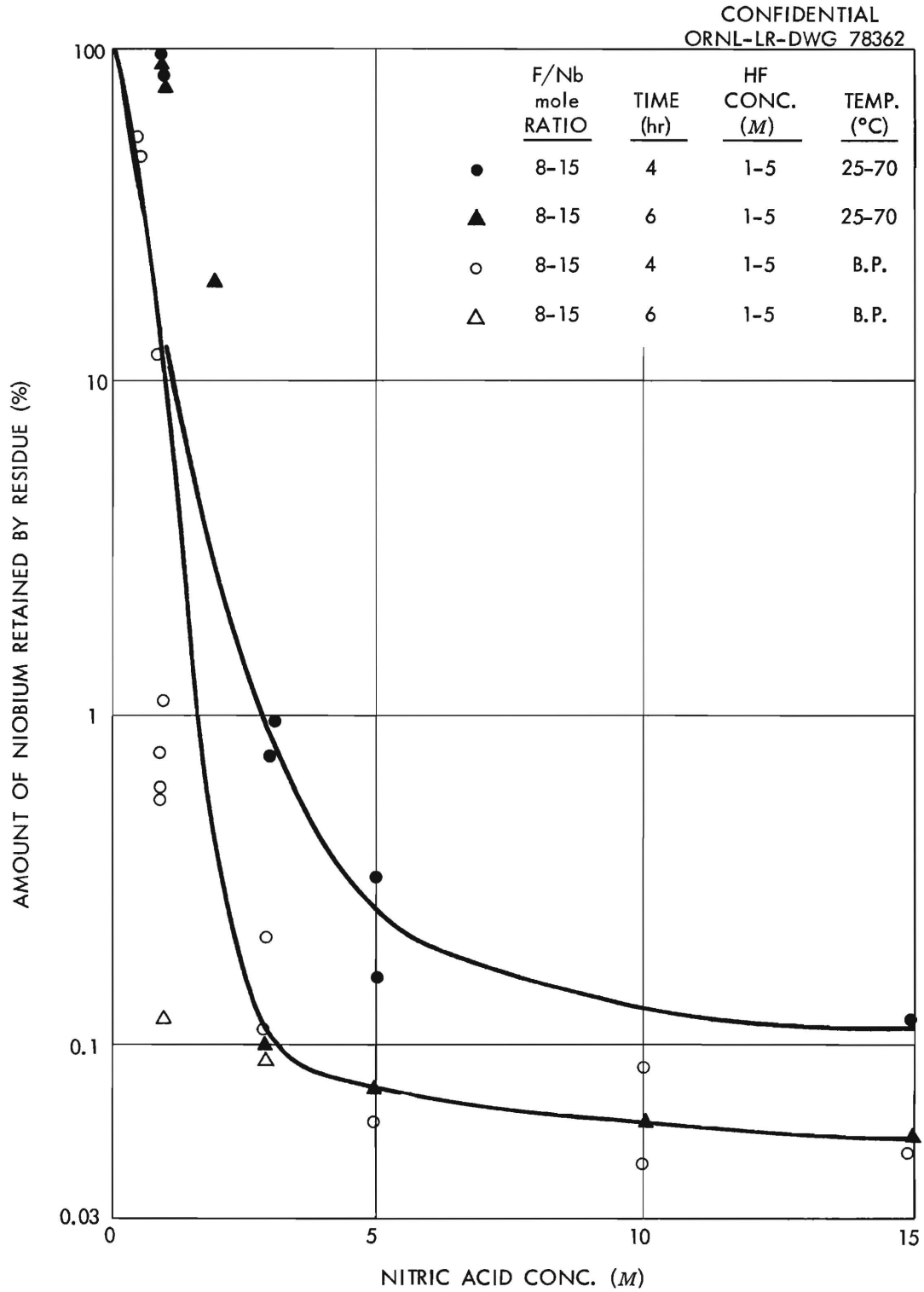


Fig. 6. Effect of Temperature, Time, and Nitric Acid Concentration on the Delining of Kiwi-B1 Fuel Samples in Nitric-Hydrofluoric Acid Solutions in Experiments Where the Overall F/Nb Mole Ratios Were 8 to 15.

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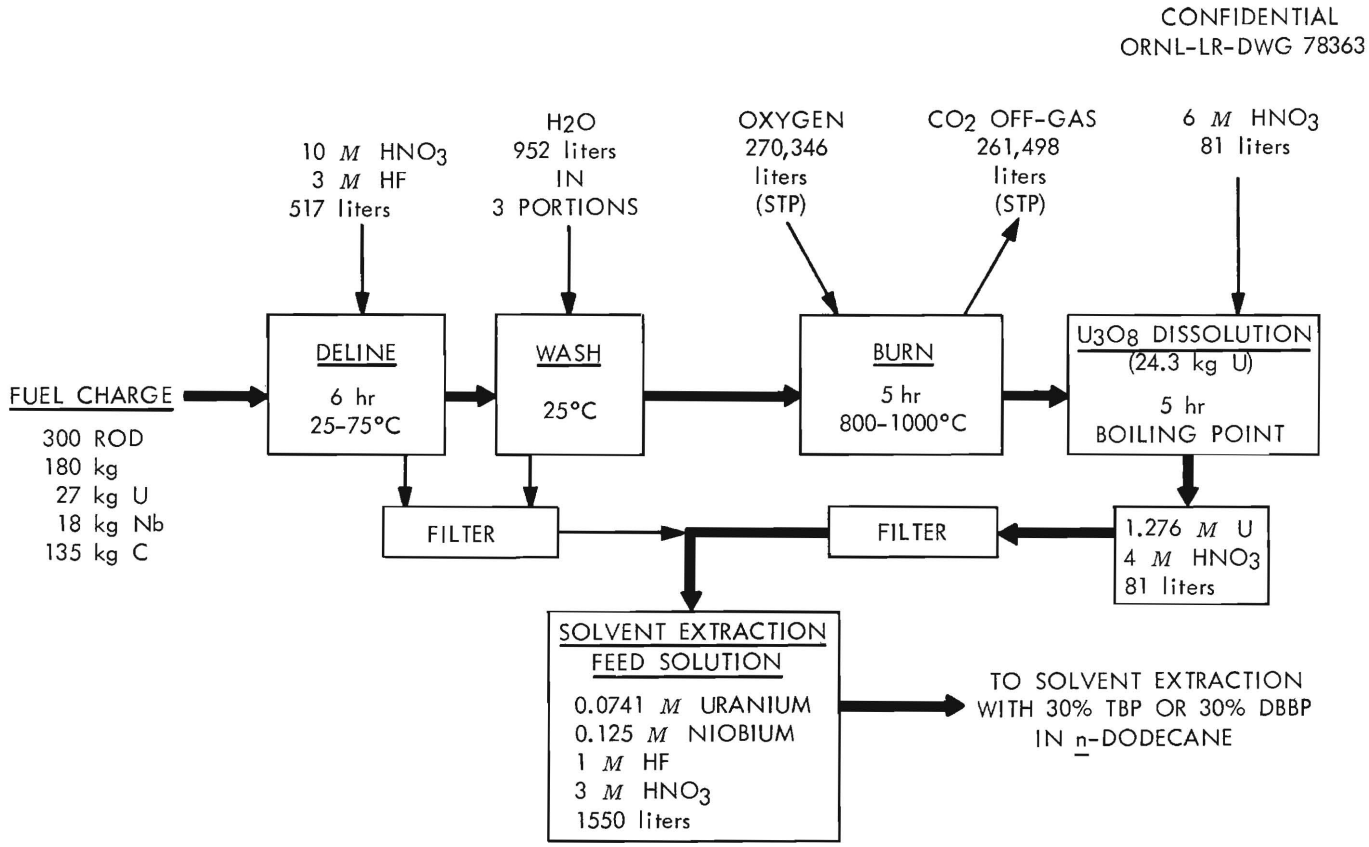


Fig. 7. Tentative Flowsheet for the Deline-Burn-Dissolve Process for Recovering Uranium from Spent Rover Fuel.

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5. Oxygen will be consumed stoichiometrically during the burning operation:

$$C + O_2 \rightarrow CO_2;\ 3UC_2 + 10\ O_2 \rightarrow U_3O_8 + 6CO_2;\ 4NbC + 9O_2 \rightarrow 2Nb_2O_5 + 4CO_2.$$

6. No attempt will be made to recover the niobium.

The major objectives of this flowsheet are to provide for maximum uranium recovery (to minimize the amount of hydrofluoric acid used) and to produce a solution from which the uranium can be recovered and decontaminated by conventional solvent extraction techniques.

There is a good possibility that the uranium from the coated particles will not migrate to the NbC liners (see assumption 2, above). In this event, the delining solution could be discarded to waste. Furthermore, with no uranium migration, fluoride could be eliminated from the process entirely by use of the Burn-Leach process (see Sec 3.2).

### 3.1.3 Experiments Based on the Flowsheet

Three laboratory-scale experiments were conducted with 35-g samples of unirradiated Kiwi-B1A fuel by following the flowsheet conditions given in Fig. 7. In each experiment, the temperature increased from 25 to about 65°C during the first 8 to 10 min of the 6-hr delining period. The F/Nb mole ratios in these experiments were between 7.8 and 9.5 (Table 4). In each case, a small amount of nitric acid-insoluble residue remained after burning the delined and washed fuel. 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 4). The compositions of the solvent extraction feed solutions were about those expected (Table 5). The variations are due to differences in the compositions of the acutal fuel and that used to calculate values for the flowsheet.

## 3.2 Development of the Burn-Leach Process

This process involves burning of the fuel at controlled temperatures in stainless steel equipment, followed by recovery of the uranium by leaching the ash with nitric acid alone. The product solution thus

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Table 4. Data from Deline-Burn-Dissolve Flowsheet Experiments with Kiwi-B1A Fuel Samples

Conditions shown in Fig. 7

| Run No. | Fuel Comp. (%) U | Nb | Fe | F/Nb Mole Ratio | $HNO_3$-Insol. Residue After Burning (% of orig. sample) | Amts. Retained by Insol. 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 |

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produced would have to be separated from the insoluble $Nb_2O_5$ by either filtration or centrifugation.

Another burn-leach experiment was conducted with a sample of simulated Kiwi-B6A coated-particle fuel. The sample was burned in oxygen for 6 hr at 800 to 900°C; then, the ash was leached for 5 hr with boiling 6 M $HNO_3$ to produce a solution about 1.4 M in uranium. The solution was separated from the insoluble $Nb_2O_5$ by vacuum filtration, and the insoluble residue contained only 0.56% of the uranium. This result is almost the same as that obtained in an experiment reported in a previous Rover monthly report.[2]

Table 5. Solvent Extraction Feed Solutions from Deline-Burn-Dissolve Flowsheet Experiments

| | Feed Solution Composition (M) | | | |
|---|---|---|---|---|
| | Uranium | Niobium | HF | $HNO_3$ |
| Calculated | 0.074 | 0.125 | 1.00 | 3.00 |
| Run 84 | 0.100 | 0.137 | 1.07 | 3.45 |
| Run 85 | 0.103 | 0.113 | 1.07 | 3.45 |
| Run 86 | 0.103 | 0.116 | 1.07 | 3.45 |

### 3.3 Combustion of Irradiated Rover Fuel

Preparations are being continued for the study of the volatility of fission products as a function of temperature during the combustion of Rover fuel. All necessary equipment, except the high-temperature furnace, has been assembled. The furnace should be available by March 1, 1963, and, at this time, the entire apparatus will be assembled and tested in preparation for the forthcoming series of hot-cell experiments.

Fuel element 1018 from the Kiwi-B4A test was transferred to the low-level cell in Building 4505 and cut into 1-in.-long sections for use in Chloride Volatility, combustion, and Fluoride Volatility experiments. Testing of the Chloride Volatility method for Rover fuel is in progress. The combustion experiments will follow, and their expected starting date is April 1, 1963.

[2]F. L. Culler, Rover Report for [redacted] 62-January 1963, ORNL-TM-509.

[redacted]

# 4. CHLORINATION AND CHLORIDE VOLATILITY STUDIES ON THE RECOVERY OF URANIUM FROM ROVER FUEL COMBUSTION ASH

## 4.1 Combustion--Hexachloropropene-Chlorination Process

T. A. Gens

A series of seven runs (Table 6) were made according to the Combustion--Hexachloropropene-Chlorination process, and a flowsheet based on the results was devised (Fig. 8). The process involves five operations, besides solvent extraction, which require a total time of about 9 hr: (1) burning the fuel elements; (2) chlorinating the product ash in hexachloropropene (HCP); (3) extraction with 3.6 M $HNO_3$ of the niobium and part of the uranium chloride dissolved in the HCP; (4) dissolution in water of the $UCl_4$ chlorination product, which is insoluble in HCP; and finally, (5) blending of the nitric acid and water solutions to obtain a solvent extraction feed solution. A preliminary investigation of the efficiency of uranium extraction with 30% TBP--Amsco from the 3 M $HNO_3$ feed solution indicated that the presence of a precipitate containing about 10% of the total niobium in the 3 M $HNO_3$ did not seriously interfere with extraction and that about seven stages would produce an extract containing 50 g of uranium per liter and a uranium loss to the raffinate of less than 0.02%.

The burning is being investigated on a small engineering scale, and results have been described in previous reports. The temperature of the burning rods will probably exceed 800°C at times, and these high temperatures will make it necessary to leave a small heel after chlorination, as discussed below.

Four liters of HCP per kilogram of ash are needed to produce nearly complete chlorination in one 4-hr treatment at the boiling point, which decreases from about 190°C initially to about 170°C after chlorination is complete. Longer chlorination is not recommended because the HCP and chlorocarbon reaction products degrade with longer heating. The HCP is removed from the insoluble $UCl_4$ product while still hot. The $NbCl_5$ product is very soluble in the hot HCP. About 98% of the niobium and up to 10%

Table 6. Flowsheet-Based Runs: Chlorination of 15.0 g of Rover Fuel Combustion Ash in 60 ml of HCP, Followed by Extraction with 3 M $HNO_3$[a] and Re-extraction with 30% Tributyl Phosphate--Amsco

Duration of HCP chlorination: Runs 1-3, 4 hr; 4-7, 3.5 hr

| Fraction | Percent of Total Uranium and Niobium in Fractions | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Run 1 | | Run 2 | | Run 3 | | Run 4 | | Run 5 | | Run 6 | | Run 7 | |
| | U | Nb | U | Nb | U | Nb | U | Nb | U | Nb | U | Nb | U | Nb |
| 3 M $HNO_3$ after TBP re-extraction | 0.005 | 91.80 | 0.013 | 93.04 | 0.006 | 87.30 | 0.004 | 85.95 | 0.006 | 89.56 | 0.010 | 81.87 | 0.003 | 97.26 |
| Material insoluble in 3 M $HNO_3$ | 0.194 | 4.75 | 0.007 | 3.20 | 0.098 | 10.67 | 0.130 | 12.30 | 0.153 | 7.70 | 0.274 | 15.78 | 0.132 | 2.36 |
| 3 M $HNO_3$ wash of insoluble material, 100 ml | 0.000 | 1.06 | 0.000 | 1.80 | 0.000 | 2.00 | 0.001 | 1.74 | 0.000 | 2.70 | 0.001 | 2.28 | 0.005[b] | 0.36[b] |
| HCP after 3 M $HNO_3$ extraction | 0.000 | 0.00 | 0.005 | 0.00 | 0.000 | 0.00 | 0.000 | 0.00 | 0.000 | 0.00 | 0.000 | 0.00 | 0.000 | 0.00 |
| 1st TBP extract, 300 ml | 89.59 | 1.48 | 84.41 | 0.94 | 85.80 | 0.04 | 90.72 | 0.04 | 85.50 | 0.04 | 87.24 | 0.07 | 90.00 | 0.02 |
| 2nd TBP extract, 200 ml | 8.63 | 0.9 | 12.94 | 0.7 | 11.67 | 0.00 | 2.80 | 0.00 | 12.00 | 0.00 | 10.43 | 0.00 | 8.68 | 0.00 |
| 3rd TBP extract, 100 ml | 1.16 | 0.0 | 1.96 | 0.0 | 1.68 | 0.00 | 5.88 | 0.00 | 1.79 | 0.00 | 1.47 | 0.00 | 0.933 | 0.00 |
| 4th TBP extract, 100 ml | 0.312 | 0.0 | 0.470 | 0.0 | 0.534 | 0.00 | 0.326 | 0.00 | 0.357 | 0.00 | 0.445 | 0.00 | 0.208 | 0.00 |
| 5th TBP extract, 100 ml | 0.077 | 0.0 | 0.133 | 0.0 | 0.156 | 0.00 | 0.110 | 0.00 | 0.148 | 0.00 | 0.104 | 0.00 | 0.053 | 0.00 |
| 6th TBP extract, 100 ml | 0.027 | 0.0 | 0.046 | 0.0 | 0.046 | 0.00 | 0.039 | 0.00 | 0.038 | 0.00 | 0.025 | 0.00 | 0.014 | 0.00 |
| 7th TBP extract, 100 ml | 0.006 | 0.0 | 0.015 | 0.0 | 0.014 | 0.00 | 0.007 | 0.00 | 0.040 | 0.00 | 0.007 | 0.00 | 0.004 | 0.00 |
| 8th TBP extract, 100 ml | --- | --- | 0.005 | 0.0 | 0.004 | 0.00 | 0.002 | 0.00 | 0.003 | 0.00 | 0.003 | 0.00 | 0.002 | 0.00 |
| 9th TBP extract, 100 ml | --- | --- | 0.002 | 0.0 | 0.002 | 0.00 | 0.001 | 0.00 | 0.000 | 0.00 | 0.001 | 0.00 | 0.001 | 0.00 |
| | Concentrations in 3 M $HNO_3$ Before Tributyl Phosphate Re-Extraction (g/liter) | | | | | | | | | | | | | |
| | 11.6 | 3.5[c] | 8.0 | 3.75 | 9.1 | 4.2 | 8.2 | 4.3 | 8.7 | 3.8 | 10.6 | 6.3 | 17.4 | 10.2 |

[a]The molarity was 3.6 to start with, but subsequent dilution with water brought it to 3 M.

[b]In run 7, the 3 M $HNO_3$ wash actually involved a 1-hr treatment at reflux, rather than a cold wash as in the other runs.

[c]Niobium concentrations were calculated by dividing the total amount of niobium, including that insoluble in 3 M $HNO_3$ (data in 2nd row) by the volume of 3 M $HNO_3$ used.

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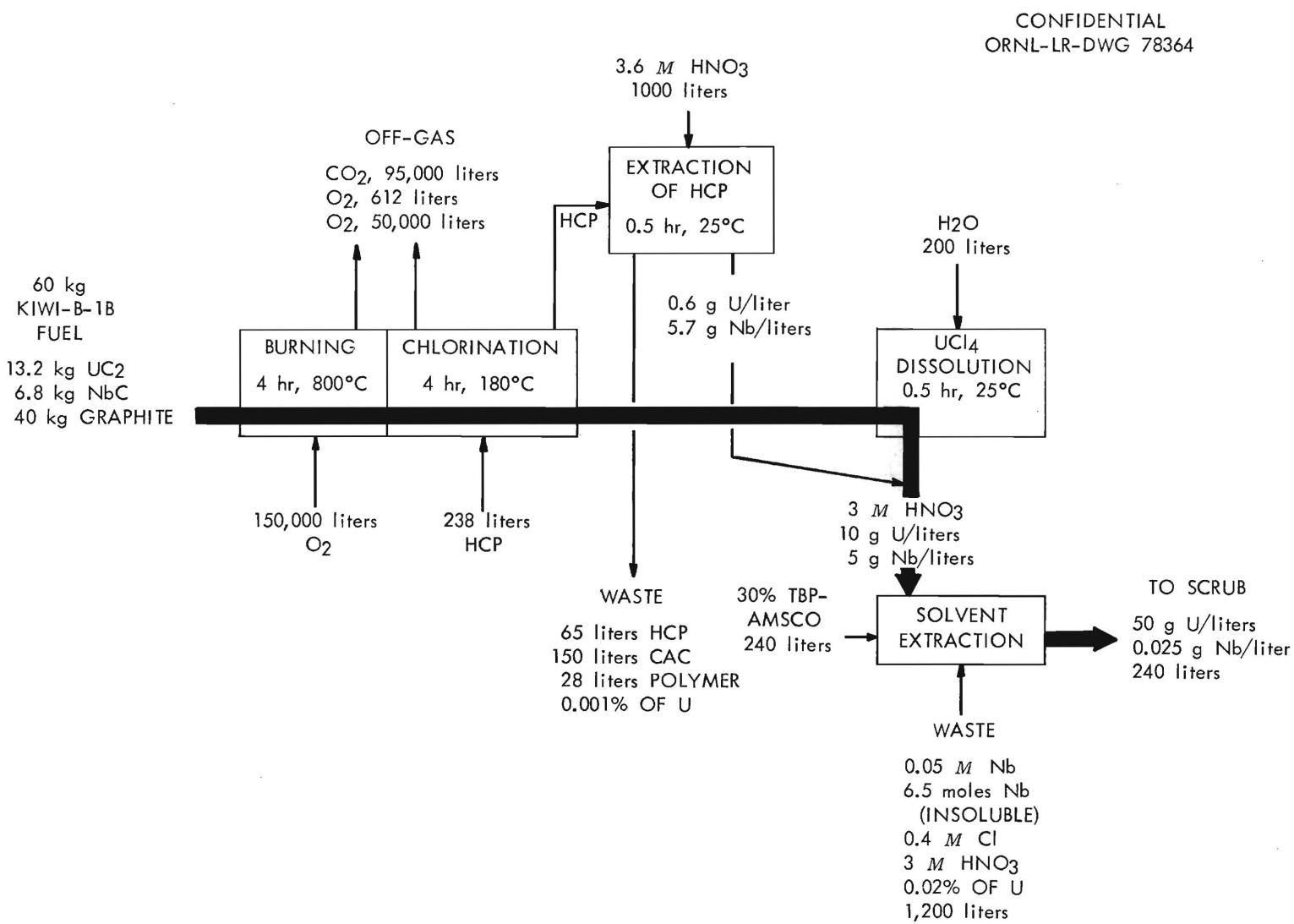


Fig. 8. Combustion–HCP Chlorination–Aqueous Extraction Process for Rover Fuel.

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of the uranium stay in the hot HCP and are extracted from the cooled HCP in a single treatment with 3.6 M $HNO_3$. If enough 3.6 M $HNO_3$ is used to yield a solution containing about 2 g of niobium per liter, all the uranium and niobium remain in this acid solution. However, if a more concentrated solution containing about 10 g of uranium and 5 g of niobium per liter is desired, it is necessary to accept precipitation of about 10% of the niobium. The latter condition was chosen for the flowsheet (Fig. 8) and the runs detailed in Table 6, in order to keep volumes low and produce a more concentrated tributyl phosphate (TBP) extract.

The $UCl_4$ precipitate is removed from the burner-chlorinator by dissolution in cold water. (Water is used, rather than nitric acid, to prevent rapid corrosion of the vessel, which would probably be made of nickel or a high-nickel alloy.) The aqueous product is blended with the nitric acid used to extract the HCP, either before or after the HCP extraction. Early runs had indicated that complete chlorination of the combustion ash could be expected and that no unchlorinated residue should be found after the $UCl_4$ dissolution. However, a small residue of unchlorinated ash, about 0.1% of the total, was found in the flowsheet-testing runs and is listed in Table 6 as material insoluble in 3 M $HNO_3$. This unchlorinated residue was carried along with the niobium precipitate through the TBP extraction in the flowsheet runs, but the amount of uranium, about 0.1% of the total in this unchlorinated material, may be too large to be discarded to waste. Therefore, this unchlorinated residue should be left in the burner-chlorinator as a heel to be chlorinated with the next run. In some cases, fused product was chlorinated, but the chlorination characteristics of the residue have not been fully defined. There is no very satisfactory method of predicting from laboratory results the behavior of these residues through several cycles of the process, since the unchlorinated residues are probably the result of sintering during burning, and the amount of sintering will depend on the conditions of burning. The separation of the unchlorinated residues from the $UCl_4$ solution does not appear difficult because the residues are dense solids.

Because about 10% of the niobium was present as a precipitate in the 3 M $HNO_3$ solution going to solvent extraction, it was necessary to make some preliminary batch solvent extraction tests, using 30% TBP--Amsco, to determine whether this precipitate would interfere with the uranium recovery. The results, shown in Table 6 as percentages of total uranium and niobium in each extract, showed that uranium extracted well, that little niobium extracted, and that the precipitate did not significantly hinder the uranium recovery. The results of runs 2 and 7, in which the uranium concentrations in the 3 M $HNO_3$ were 8 and 17 g/liter, respectively, when plotted on a McCabe-Thiele diagram (Fig. 9), indicated that about ten and seven solvent extraction stages, respectively, would be needed to produce an extract containing 50 g of uranium per liter at a loss of less than 0.02% to the raffinate, at an assumed operating ratio of 1 liter of 30% TBP--Amsco to 5 liters of 3 M $HNO_3$.

The presence of 0.4 M chloride in the solvent extraction feed makes it necessary to use chloride-resistant materials, such as titanium. Glass equipment was used in the laboratory work. A scrub with strong nitric acid is necessary to remove chloride dissolved in the TBP--Amsco. A summary report on this work was written and is now in process.[3]

If desired, nearly half the HCP can be recovered by distillation from the chlorocarbon waste. There are three distinct fractions in this waste, one boiling at about 165°C, which is apparently the trichloroacrylyl chloride chlorination product (CAC), the HCP boiling at about 210°C, and higher-boiling material, which represents about 10% of the original volume of the HCP.

## 4.2 Corrosion Tests Relating to Chlorination with Hexachloropropene

W. E. Clark

Exposure of type 304L stainless steel in refluxing hexachloropropene, with and without dissolved $U_3O_8$, resulted in maximum corrosion rates of less than 0.4 mil/month for a 24-hr exposure. Continuing the

[3] T. A. Gens and T. B. Borne, Laboratory Development of a Process for Recovering Uranium from Rover Fuel by Combustion, Liquid-Phase Chlorination with Hexachloropropene, and Aqueous Extraction, ORNL-3435 (in process) (Confidential).

[redacted]



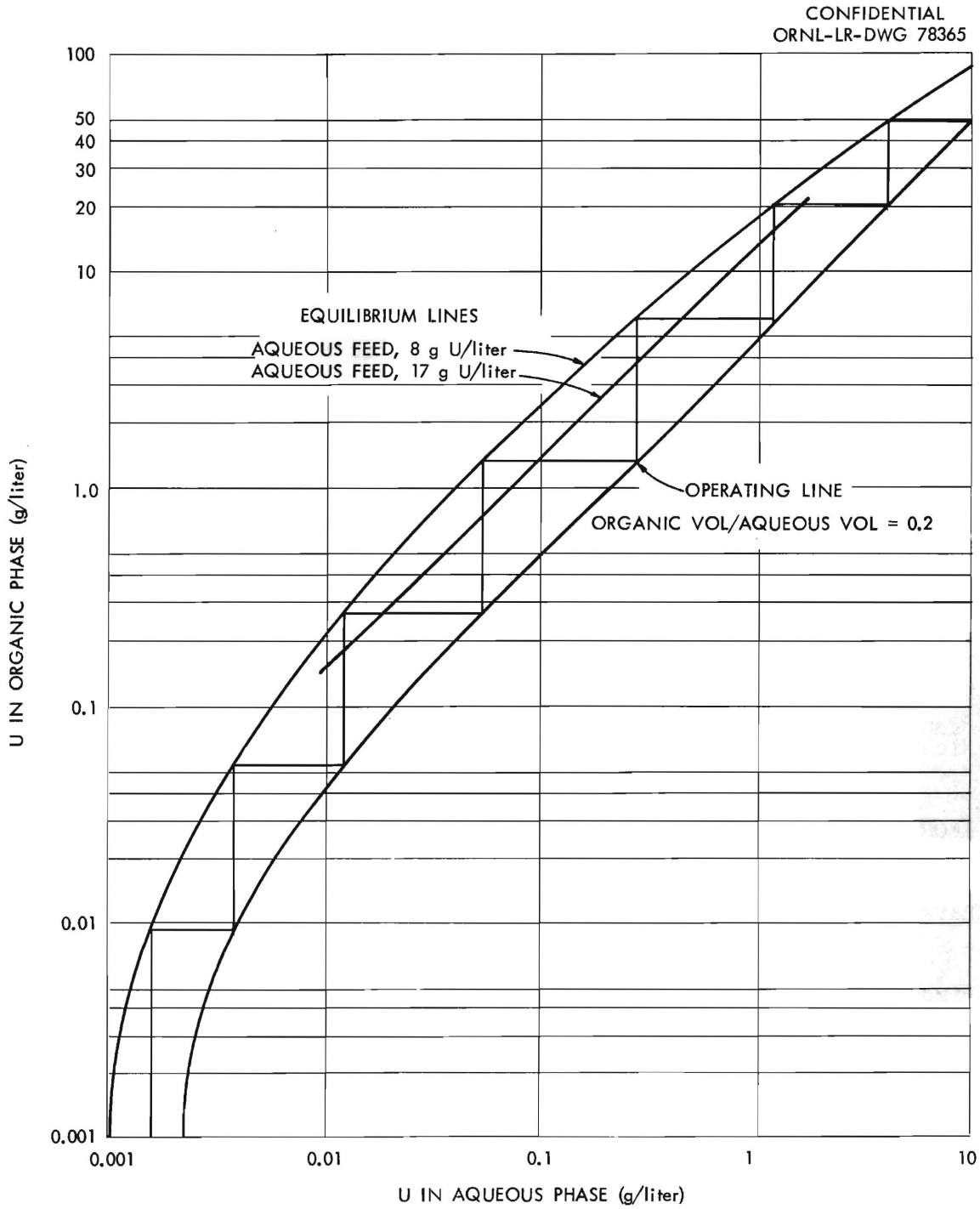


Fig. 9. Stage-Concentration Diagram for Extracting Uranium from the Hexachloropropene Extract with Tributyl Phosphate–Amsco Mixture.

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exposure for 264 hr in the solution that contained dissolved $U_3O_8$ resulted in decreasing the overall rate to 0.12 mil/month for 264 hr of exposure. "A" nickel, Haynes 25, Nichrome V, and INOR-8 also showed rates that decreased with time, the 264-hr rates varying from 0.02 mil/month for Haynes 25 to 0.08 mil/month for Nichrome V (Table 7). The corrosion rates for niobium and tantalum were more or less constant with time, at 0.5 to 1.0 and 0 to 0.09 mil/month, respectively. The selection of a container material for hot hexachloropropene, with or without dissolved uranium, appears therefore to present no problem.

Table 7. Cumulative Corrosion Rates in Refluxing Hexachloropropene (HCP) Systems

| | | Corrosion Rate (mil/month) | | | |
|---|---|---|---|---|---|
| | Location of | In HCP for | In HCP Containing 280 g of Dissolved $U_3O_8$ for: | | |
| Material Type | Specimen | 48 hr | 24 hr | 168 hr | 264 hr |
| 304L stainless steel | Vapor | 0.2 | 0.37 | 0.04 | 0.04 |
| | Solution | 0.0 | 0.16 | 0.06 | 0.05 |
| "A" Nickel | Vapor | | 0.0 | 0.04 | 0.04 |
| | Solution | | 0.28 | 0.06 | 0.05 |
| Nichrome V | Vapor | 0.2 | 0.15 | 0.11 | 0.08 |
| | Solution | 0.0 | 0.14 | 0.03 | 0.03 |
| INOR-8 | Vapor | <0.1 | 0.06 | 0.01 | 0.01 |
| | Solution | 0.0 | 0.05 | 0.01 | 0.01 |
| Haynes 25 | Vapor | 0.1 | 0.03 | 0.01 | 0.02 |
| | Solution | 0.0 | 0.0 | 0.01 | 0.01 |
| Nimonic 75 | Vapor | 0.1 | | | |
| | Solution | 0.0 | | | |
| Niobium | Vapor | | 0.50 | 0.23 | |
| | Solution | | 0.85 | 0.95 | |
| Tantalum | Vapor | | 0.0 | 0.01 | |
| | Solution | | 0.09 | 0.05 | |