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DEVELOPMENT OF PROCESSES AND EQUIPMENT FOR
RECOVERING URANIUM FROM ROVER-FUELS-BURNER ASH

G.W. Hogg, J.A. Rindfleisch, P.E. LaMont,
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ABSTRACT

Development of processes and equipment for recovering uranium from nuclear rocket (Rover) fuels is described. Secondary burning of primary ash, ash dissolution, liquid-solids separation, startup and supplemental heating of fluidized-bed burners, and other related development areas are discussed. Recovery of greater than 99.8% of the uranium from the ash was demonstrated in the pilot plant.

SUMMARY

Pilot-plant development of a process for recovering uranium from Rover fuels has been completed at the Idaho Chemical Processing Plant (ICPP). The process includes: (1) continuous primary burning of Rover fuel, (2) secondary batch burning of primary burner ash to reduce its carbon content, (3) batch dissolution of the secondary-burner ash using sequential 8 M HNO_3 and 8 M HF dissolution steps, (4) separation of the undissolved solids from the dissolver effluent, (5) washing of occluded uranium from the undissolved solids, and (6) collection of the undissolved solids for disposal. The solids-free uranium-bearing liquid effluent is fed to an existing TBP solvent extraction system. This report emphasizes development of the secondary burning, dissolution, and solids-liquid separation processes; primary burning has been emphasized in a previous report⁽¹⁾.

Pilot-plant results show that: (1) the carbon content of primary burner ash can be reduced to less than 2% by weight by secondary burning, (2) the Al_2O_3 elutriated in the secondary-burner ash is less than 1% of the total ash, (3) 99.8% of the uranium and 70% of the Nb can be dissolved in a 3.5-hour leaching period, (4) the dissolver solution can be accurately complexed with $\text{Al}(\text{NO}_3)_3$, (5) the dissolver solutions are stable, (6) greater than 90% of the undissolved solids can be separated in a settling tank, (7) reliable dry solids transfer can be maintained using gas purges and vibrators, and (8) due to the corrosiveness of the HNO_3 - HF solution, it is necessary to line the dissolver with plastic.

The pilot-plant secondary burner, dissolver, and solids-liquid separation equipment were interfaced to demonstrate combustion, dissolution, and separation efficiencies when operated in-line. The results of the in-line operations confirmed the performance obtained for the individual equipment components.

Heat transfer calculations were made that showed the primary and secondary burners could be heated from ambient to 760°C in less than 20 hours using external electrical heaters. The calculations showed that sufficient heat transfer area and heater space are available to ensure allowable burner surface temperatures will not be exceeded.

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I. INTRODUCTION

The reprocessing of spent Rover* fuel elements requires combustion of the graphite fuel matrix followed by dissolution of the burner ash to recover uranium. The development of a burner for the initial continuous combustion of Rover fuel (primary burning) has been reported elsewhere.⁽¹⁾ The development of processes and equipment to recover uranium from the primary ash involved studies of secondary burning, solids transfer, dissolution, and liquid-solids separation. This report is a collection of sub-reports describing the work performed in individual ash-processing-development areas. The primary purpose of the development effort reported herein was to provide design criteria⁽²⁾ for the Rover Fuels Reprocessing Plant to be installed at the Idaho Chemical Processing Plant (ICPP).

* Note:

Some documents published previously refer to these fuels as nuclear rocket fuels. As used in this report, the terms rocket, Rover, and highly enriched uranium graphite fuels are synonymous.

II. SECONDARY BURNING

Elutriated ash from the continuous fluidized-bed burner⁽¹⁾ (primary burner) contains 15 to 25% carbon. Carbon content must be reduced to less than 2% to prevent excessive frothing during dissolution.

A preliminary investigation of secondary burning showed that the unburned carbon in the elutriated primary ash could be reduced to less than 1% by batch combustion in a bed of alumina (Al_2O_3) particles fluidized by pure oxygen. Additional secondary burning and elutriation studies were then necessary to firmly identify the secondary-burner design features and operating conditions that result in product ash containing less than 2% carbon and less than 1% Al_2O_3 .

Test Objectives

The experimental objectives associated with secondary burning studies were as follows:

1. Reduce the carbon content of the primary ash to less than 2% within a 1.5-hour period by combustion with O_2 .
2. Elutriate ash from the secondary burner into a collection vessel during a 1.5-hour period with less than 1% carryover of alumina.
3. Charge primary burner ash to the secondary burner through a double hall-valve charging system without plugging the charge line.

Test Equipment

A schematic of the pilot-plant secondary burner, including charging valves and a product collection pot, is shown in Figure 1. The fluidizing vessel was a 2-inch diameter Hastelloy C pipe expanding to a 4-inch diameter stainless steel disengaging section. The disengaging section contained a sintered-metal filter for removal of particulates from the off-gas during the combustion step. A stainless steel product collection pot containing a sintered metal filter was used during the product elutriation step. The 1/2-inch charging tube extended below the filter to prevent the accumulation of freshly charged solids on the top surface of the filter. The secondary burner system was assembled

and installed in a walk-in hood. The combustion process was monitored by continuously measuring the levels of CO and CO₂ in the off-gas.

Preliminary Tests

Two preliminary tests were conducted to check the operation of the equipment and to correct design and operating deficiencies. Since previous experience showed that the holdup of uranium can be significant on a fresh bed of alumina and in dead spaces in the system, initial charges were necessary to "saturate" the bed with uranium so that greater uranium recovery could be obtained during subsequent runs. The two tests are described as follows:

Test 1: A 200 g sample of primary ash was charged to the burner; the burner contained 1 kg of fresh 60-mesh alumina, which was fluidized by air at 500°C. The charging tube was plugged by a solids bridge, which was removed by "rodding out" the tube. The system was then fluidized by oxygen at 0.85 ft/sec and heated until combustion began. Combustion preceeded smoothly without exceeding a bed temperature of 800°C. After complete combustion, fluidizing air was used to elutriate ash; however, the ash could not be separated from the bed material because the elutriation line was too near the top of the fluid bed. Following the run, the charging tube was modified to permit pressurization by nitrogen in order to break solids bridges, and the elutriation line was moved upward to the disengaging section. (Although a larger diameter charging tube was desired, major modifications would have been required.)

Test 2: Product from Test 1 was charged to the final bed from Test 1; no charging problems were encountered. At a bed temperature of 500°C, an elutriation test was conducted for one-hour periods at 0.85 and 1.3 ft/sec, respectively. Only a small quantity of product (19 and 23 g) was collected at each condition; however, no significant quantity of bed material was found in the product. Primary ash (200 g) was then charged to the burner; combustion began when the operating temperature was near 620°C using fluidizing oxygen. Combustion subsided within 1.5 hours; product ash was then elutriated for two one-hour periods at 0.85 and 1.3 ft/sec, respectively. The ash contained less than 1% each of unburned carbon and alumina.

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Figure 1. - Schematic Diagram of Pilot-Plant Secondary Burner

Pilot-Plant Demonstration

A pilot-plant demonstration which consisted of processing three batches of primary ash sequentially through the secondary-burning, ash-dissolution, and liquid-clarification steps was conducted. Expected plant-scale operating conditions were closely simulated where practical. The three secondary burner runs (Tests 3, 4, and 5) proceeded smoothly during the demonstration; all experimental objectives were achieved. The final bed from Test 2 (~1 kg) was the starting bed; the total weight of each charge of primary ash was 300 g or less in order not to exceed the 400 g limit for uranium in the walk-in hood. Other experimental conditions are summarized in Table I. Results from the pilot-plant demonstration tests are summarized in Table II.

TABLE I

PILOT-PLANT SECONDARY BURNER OPERATING CONDITIONS

	Operating Mode		
	Charging	Combustion	Elutriation
Fluidizing Gas	air	O ₂	air
Fluidizing velocity, ft/sec	0.85	0.85	1.3
Bed temperature, °C	<600	600 - 800	<800
Period, hr.	0.1	1.0	1.5

TABLE II

EFFECT OF SECONDARY BURNING ON ASH COMPOSITION

		Test Number		
		3	4	5
Primary Ash	Weight, g	250	300	300
	Combustible, %	17	18	24
	Uranium, g	117	96	71
	Niobium, g	45	77	86
Secondary Ash	Weight, g	166	224	223
	Combustible, %	---	1.01	1.24
	Charge to Dissolver, g	166	200	200

The pilot-plant results pertaining to the three secondary burner operations of charging, combustion, and elutriation are described and related to the plant secondary-burner design and operation.

1. Charging: Pressurization of the charging pot was effective in preventing solids bridging of primary ash in the 1/2-inch diameter (pipe) charging tube. Even though primary and secondary ash have been easily charged through 1-inch diameter pipes, the plant-scale charging vessel and secondary ash collection vessel should be equipped for low level pressurization (using 5 to 10 psig nitrogen to prevent combustion in the charging tube) to prevent solids bridging. The plant-scale secondary burner charging tube should extend downward to well below the in-vessel sintered-metal filters to prevent contact and possible burn-through by combustion of primary ash.

2. Combustion: The ignition temperature of primary ash in the secondary burner fluidized by O_2 was approximately $620^{\circ}C$ in all five runs. Therefore, primary ash could be charged to the plant-scale burner at $600^{\circ}C$ while fluidizing with air. Oxygen can be used for fluidization after combustion is started under controlled conditions with air. (If the ignition temperature is less than $620^{\circ}C$, the charging temperature should be reduced correspondingly.) The use of air to initiate combustion is intended to prevent a temperature excursion resulting from the high combustion rates possible when fluidizing with pure O_2 .

The average specific carbon combustion rate during the pilot-plant demonstrations was 2.4 kg C/hr-ft^2 of cross-sectional area; actual combustion rates were much greater for a short period of time. Heat transfer rates could limit the specific combustion rate in the plant-scale secondary burner to approximately 5 kg C/hr-ft^2 ; however, combustion rates up to 13 kg C/hr-ft^2 can occur with O_2 fluidization. Mixing of fluidizing O_2 and air might be required to slow combustion rates; the combustion period would then be lengthened to 2-4 hours. Cooling air was introduced above the bed to prevent the sintered metal filters from exceeding their design limit of $537^{\circ}C$; in the plant-scale secondary burner, the fluidizing gas must be cooled either by a heat exchanger or by dilution air prior to contacting the filters.

3. Elutriation: The elutriation velocity shown in Table I was the superficial velocity in the 2-inch diameter fluidizing vessel; the corresponding velocity in the larger-diameter disengaging section was 0.45 ft/sec. Under these conditions, excellent separation of product ash from bed material was obtained; only 2.9 g of alumina were elutriated with the secondary ash during the entire demonstration. Additional evidence of clean separation of secondary ash from the bed was the close agreement of equivalent U_3O_8 plus Nb_2O_5 in the dissolvent with the weight of the secondary ash charged to the dissolver.

An additional elutriation test was made at the end of Test 5 in which product was collected for two one-hour periods at superficial velocities of 1.5 ft/sec and 1.75 ft/sec, respectively. The solids analyses showed gross quantities of bed material were carried over into the product take-off line. Therefore, a fluidizing velocity during elutriation of 1.3 ft/sec is recommended for the plant-scale burner.

Uranium and Niobium Material Balances

Uranium and niobium material balances during secondary burning in all five runs are shown in Table III. As expected, uranium recovery was low when starting with a fresh bed of alumina, but recovery improved with succeeding charges. Based on the results of these few runs, it appears that a continuous buildup of uranium as a coating on the bed material will not occur. On the other hand, niobium showed a greater tendency for retention in the bed. Accumulation of niobium in the plant secondary burner at the rate realized in the pilot-plant demonstration could not be tolerated; therefore, control of niobium accumulation by jet grinders and/or bed replacement will be required with the plant-scale system.

Conclusions and Recommendations

The following conclusions and recommendations are based on the results of secondary-burner operations during the pilot-plant demonstration.

1. The three essential operating steps of primary ash charging, batch combustion using fluidizing oxygen, and elutriation of secondary ash using fluidizing air can be readily accomplished using a bed of fluidized alumina particles.

TABLE III

URANIUM AND NIOBIUM RECOVERY DURING SECONDARY BURNING

Test	Uranium			Niobium		
	Charged, g	Recovered, g	% Recovered	Charged, g	Recovered, g	% Recovered
1	93.8	27.3	29.1	36.2	10	27.6
2	93.8	73.0	77.8	36.2	21.3	58.8
3	117.2	104.5	89.2	45.2	28.2	62.4
4	96.3	107.4	111.5	77.2	66.1	85.6
5	70.9	117.5	165.7	86.2	97.9	113.6
Total	472.0	429.7	91.0	281.0	223.5	79.5

2. Operating conditions recommended for the plant-scale secondary burner are similar to those shown in Table I, except that a combustion period of 2-4 hours with O_2 -air mixture is required, and an elutriation velocity of less than 1.3 ft/sec might be satisfactory.
3. The average specific combustion rate during the demonstration was 2.4 kg C/hr-ft² of bed cross sectional area. The maximum stoichiometric rate while fluidizing with O_2 at 0.85 ft/sec is approximately 13.6 kg C/hr-ft²; therefore, the capacity of the pilot-plant secondary burner was considerably greater than realized in the pilot-plant demonstration. The specific combustion rate recommended for the plant-scale secondary burner should not exceed 5 kg C/hr-ft² to eliminate the possibility of temperature excursions.
4. The buildup of uranium in the pilot-plant secondary burner was small after the first few charges of primary ash; however, niobium buildup was significant. Jet grinders are recommended for the plant-scale burner for slowing and/or preventing niobium buildup; periodic bed removal may be required for niobium control.

III. ASH DISSOLUTION

The ash dissolution studies conducted at ICPP consisted of defining the Rover plant dissolution flowsheet and process equipment development through pilot-plant demonstration.

1. LABORATORY DEVELOPMENT OF DISSOLUTION FLOWSHEET

During primary burning, NbC is converted to Nb_2O_5 which combines with uranium to form nitric acid insoluble niobium uranate (Nb_3UO_{10}). The Nb_3UO_{10} requires HF for dissolution. Although a HNO_3 -HF dissolution process is established for fuels containing similar compounds (specifically zirconium), the stability limits, reaction time, and corrosiveness of the various dissolvent, dilution, and complexing solutions were not known specifically for Nb_3UO_{10} and Nb_2O_5 . Also, a soluble neutron poison is required for the dissolution process to be critically safe. A knowledge of the effect on stability and homogeneity of the soluble poison in the various solution matrices was also required.

Objective of Study

The primary objective of the laboratory study was to develop a flowsheet, compatible with existing plant equipment, for recovering at least 99.5% of the uranium during the processing of Rover fuel. Other specific objectives were: (1) to establish conditions for minimizing undissolved solids while maintaining stable solutions during all process steps, (2) to evaluate corrosion problems associated with the flowsheet, and (3) to establish the corrosion and stability effects of a soluble neutron poison in the dissolution streams.

Flowsheet

The flowsheet conceived (Table IV) is similar to those now used at the ICPP for zirconium dissolution. The Rover and zirconium processes are analogous in that hydrofluoric acid is required to dissolve all of the fuel meat; complexing of the excess hydrofluoric acid is also required.

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[illegible]

The Rover plant flowsheet is based on a fuel charge of 200 kg/d and a three-batch per day dissolution cycle. This results in processing an average of 10 kg of uranium and 6.7 kg of niobium per batch dissolution.

Experimental Conditions

Secondary burner product ash was dissolved at 70-80°C using a sequential acid dissolution. During the dissolution, an 8 M HNO₃-3.5 g/l boron solution at 75°C was mixed with the ash for 30 minutes, followed by dilution with borated water and mixing with 28.4 M HF-3.5 g/l boron solution. All reagents were heated to 75°C before addition to minimize the dissolution time. The nitric acid reacted vigorously with the product ash at 75°C. The HF and HNO₃ solutions can not be added to the dissolver simultaneously because of the formation and precipitation of UO₂F₂. Also, the HF solution can not be added to the dissolver before the HNO₃ solution is added because hydrofluoric acid forms a UF₄ coating on the U₃O₈ particles, restricting the uranium dissolution substantially.

The nitric acid fraction of the leachate cannot be processed separately from the hydrofluoric acid fraction for three reasons:

1. A colloidal solid (Nb₃UO₁₀) is present in the solution that must be separated by centrifugation or filtration. These solids, in the plant-scale system, would have to be returned to the dissolver vessel for the HF dissolution, thus, requiring more time for dissolution and handling.
2. The nitric acid fraction alone would be of insufficient volume for operating the extraction columns in the plant-scale system.
3. During plant operation, economical advantage exists in processing the hydrofluoric-acid fraction with the nitric-acid fraction from the standpoint of materials and personnel.

If hydrofluoric acid is added directly with the nitric acid, a complex of uranium and fluoride precipitates. This condition is undesirable from a criticality viewpoint as well as impairing the dissolution by preventing effective contact of the acids with the solids. The dissolution efficiency is also decreased, since the fluoride is

"tied-up" by the uranium. This precipitation problem was eliminated by the addition of borated dilution water before the addition of hydrofluoric acid. The graph in Figure 2 shows the relationship between required dilution water and uranium in 8 M HNO_3 -3.5 g/l boron solution to prevent the uranium-fluoride precipitate. Since 450 g/l uranium is the maximum concentration to be expected, 20% more boron dilution water is added to prevent the formation of the uranium-fluoride precipitate. The addition of a dilute solution of hydrofluoric acid (instead of dilution water) to give the same volume and concentration of solution does not prevent the undesirable precipitation. The original leach solutions are of sufficient quantity to contain more acid, by a factor greater than 2, than is necessary for the stoichiometric reaction with the product-ash constituents. This speeds the reaction and assures dissolution and stability during minor increases in niobium and/or uranium content of the secondary ash.

Greater than 99.9% dissolution of the uranium and 80% dissolution of the niobium was obtained with the flowsheet (Table IV). The niobium dissolution rate is dependent on the fluoride concentration and reaction temperature as shown in Tables V and VI. The higher the fluoride concentration and temperature, the faster the niobium dissolution. However, increases in fluoride concentration require an increase in complexer volume and, consequently, a higher cost for waste disposal. Since total dissolution of the niobium is not required for uranium recovery, approximately 70% niobium dissolution at a temperature of 75°C was selected to minimize solids handling problems while obtaining 99.9% uranium recovery.

Complexing the Dissolver Product

After dissolution, any excess fluoride (i.e., that which is not complexed) must be complexed to reduce the corrosion potential of the dissolver product solution. This particular step is probably the most crucial of the entire flowsheet. If the amount of aluminum present exceeds the fluoride concentration in the dissolver solution, the aluminum breaks the Nb-F complex causing Nb_2O_5 to precipitate. If the solution is undercomplexed, AlF_3 tends to precipitate because of the high fluoride-to-aluminum ratio, and the solution remains corrosive.

Figure 2. - Borated Dilution Water Required to Prevent Uranium-Fluoride Precipitation During Dissolution

TABLE V

EFFECT OF FLUORIDE CONCENTRATION ON PERCENT Nb DISSOLVED

Sample	1	2	3	4
Fluoride Conc. <u>M</u>	4.3	7.9	10.8	13.6
Nb ₂ O ₅ , %	23.7	23.7	24.3	25.0
Undissolved Solids, %	17.8	15.4	13.1	9.5
Nb Dissolved, %	61.3	71.2	81.1	100
Dissolution Time, hrs.	4	4	4	4

TABLE VI

EFFECT OF TEMPERATURE ON PERCENT Nb DISSOLVED

Sample	1	2	3	4
Temp., °C	60	70	80	95 (boiling)
Fluoride Conc., <u>M</u>	7.9	7.9	7.9	7.9
Nb ₂ O ₅ , %	23.4	23.2	23.6	25.9
Undissolved Solids, %	13	10	10	4.7
Nb Dissolved, %	60	71	72	96
Dissolution Time, hrs.	4	4	4	4

Laboratory studies were made to find a stable complexed solution by mixing portions of the uncomplexed dissolver product solution with specified portions of 2.2 M aluminum nitrate - 3.5 g/l boron solution. The guideline for complexing was established by the use of a fluoride electrode which measures "free fluoride". The theoretically calculated "free fluoride" of the stable complexed system must be maintained at approximately 0.9 M in order to obtain stability. The theoretical "free fluoride" was calculated using equation (1).

$$(1) \text{ "Free Fluoride" } = (\text{total fluoride}) - (1.7 \text{ Al} + 0.2 \text{ U} + 4.0 \text{ Nb} + 3.4 \text{ B})$$

As shown by the equation, niobium and boron are the major complexing elements. The stoichiometric complexing values given in the equation are the best to date of the true estimate of fluoride complexing in the system. However, because of interaction in such a complex solution, the above equation may not give a true representation of the "free fluoride" present. This possibly explains why a high concentration of "free fluoride" is calculated, even though it may be substantially lower, to maintain a stable solution. The stability of the solution is dependent on six variable concentrations: acid, aluminum, fluoride, uranium, niobium, and boron; any of these can cause instability. Because of this complex interdependence, each dissolver solution is unique, and a simple equation cannot guarantee corrosion-free, stable, solutions. Niobium is the key to complexing the fluoride, because the concentration of all the other constituents of the stream remain relatively constant with the exception of the uranium; uranium complexing is insignificant compared to the other constituents. Therefore, "free fluoride" concentration is primarily dependent on the niobium concentration. Niobium can be either in the form of Nb_2O_5 or $\text{Nb}_3\text{UO}_{10}$, and equations (2) and (3) show the amount of hydrofluoric acid required to dissolve each compound.

If there should be some loss of fluoride or an error in makeup or addition, the solution can become unstable, corrosive, or both. The fluoride electrode eliminates the "guess work" of complexing.

By titrating a sample of the dissolver solution with the aluminum nitrate to be used for complexing, a curve is obtained showing how much aluminum nitrate to add per given volume of dissolver solution. Knowing the total volume of dissolver solution, the required amount of complexer solution can be calculated. The value from the curve, as shown in Figure 3, is taken as 1 ml before the break, thus, allowing for the slow boron-fluoride reaction and to maintain the small amount of fluoride necessary to insure stability with minimum corrosion.

Solids Handling

The dissolution of Rover ash produces undissolved solids in the dissolver product; the solids consist of <6 kg/d of niobium oxide and <2 kg/d of aluminum oxide; there will be small quantities of carbon. The bulk of the solids must be removed before the solution can be transferred to the first-cycle extraction columns. These solids, if allowed to enter the columns, would possibly cause emulsion formations, resulting in column upsets and possible uranium losses. The complexed dissolver slurry is transferred directly to a settling tank and subsequently to a centrifuge where the remaining residue is separated from the solution.

Corrosion

A preliminary study of the anticipated corrosion rate in the plant centrifuge (304L stainless steel) was conducted which showed a corrosion rate of less than 2.0 mil/month.

IBR Complexing

After the uranium is extracted into the organic phase, the organic phase is scrubbed with an aqueous solution. The resulting solution, the IBR stream, contains residual amounts of uranium that require recovery. The IBR is mixed with the feed stream and recycled through the extraction columns. This presents some difficulty in the proposed Rover flowsheet, because the IBR contains aluminum nitrate which will cause severe instability in the complexed dissolver product. There are two ways to solve this problem: (1) the complexed dissolver product can be mixed with a solution of hydrofluoric acid and nitric acid in proportions necessary to counteract any instability and complex any aluminum nitrate introduced by the later addition of the IBR stream, or

Figure 3. - Typical Curve for Complexing Fluoride with Aluminum in a Complex Matrix

(2) the IBR stream can be placed in a feed adjustment vessel where the HF and HNO_3 can be mixed with the IBR as the acid addition occurs, in which case all of the fluoride will be complexed immediately. The complexed dissolver solution can then be mixed with this resulting solution directly from the centrifuge without concern for stability. Of these options, it would appear that the second method would be superior because of corrosion problems of the HF- HNO_3 mixture before complexing with the aluminum in the IBR. The combined solutions could then go to the input measurement tanks ready for extraction.

Criticality Safeguard

During dissolution, it is necessary to add a neutron poison to prevent a critical mass from occurring. Boron in the concentration of 3.5 g/l is used in all solutions in the dissolver vessel and in all streams that are added to the vessel. A possible crucial requirement for this system in terms of criticality is to prevent the uranium-fluoride complex from precipitating. However, if the precipitate occurs, laboratory analyses show that the boron does stay in solution. The flow-sheet must be examined by safety review personnel to ascertain whether the boron is sufficient for criticality safety. If not, then $\text{Cd}(\text{NO}_3)_2$ can possibly be added to give added safety to the system.

Conclusions

The results of the laboratory dissolution studies show:

1. 99.8% of the uranium in the Rover fuel can be recovered.
2. Any desired amount of niobium can be dissolved by increasing the hydrofluoric acid concentration.
3. A flowsheet was developed that produced stable solutions throughout the dissolution cycle.
4. Anticipated corrosion rates of less than 10 mils per month in the centrifuge appear acceptable considering the short campaign for Rover fuels reprocessing.
5. The extraction feed stream is compatible with existing plant extraction equipment.
6. The amount of undissolved solids (Nb_2O_5 , Al_2O_3 , and C) should not exceed 9 kg per day.

2. PILOT-PLANT DISSOLUTION STUDIES

The primary objective of the Rover dissolution process development is recovery of greater than 99.8% uranium in the pilot plant and greater than 99.5% of the uranium contained in Rover fuel during the plant-scale operations. Minimization of uranium loss is an obvious operating criterion for economic reasons alone. Additional incentive for high uranium recovery lies in the need for minimizing the generation of alpha-active waste.

The dissolution process must be flexible enough to meet all process requirements over the anticipated throughput and composition ranges of the ash. Although the proposed fuel charging rate to the primary burner is a constant 200 kilograms per 24 hours, ash composition (due to holdup in the burners, etc.) can vary widely.

The dissolver product must be chemically stable, i.e., form no precipitates for a specified length of time following discharge from the dissolver. Solution stability is required both to prevent processing problems, e.g., solids buildup in lines, columns, and valves, and to avoid mass accumulations which could pose a nuclear criticality hazard.

Additional process requirements are: (1) the leachate must result in low corrosion rates, preferably < 3 mpm in processing equipment downstream of the dissolver, (2) the process must be free of criticality hazards, (e.g., adverse geometry, high uranium concentrations), and (3) all material transfers to and from the dissolver must be simple and relatively trouble-free.

Equipment Description

The Rover dissolution pilot plant was constructed to simulate a plant-scale installation meeting the processing requirements detailed in the preceding section. Solids and liquid transfer and mixing techniques were selected for compatibility with remote-facility plant practice. The pilot-plant is shown schematically in Figure 4.

The dissolver vessel was a 3-inch diameter, 36-inch long, right-cylindrical vessel constructed of low-density polyethylene. Polyethylene was selected both for ease of construction and to withstand the range of

Figure 4. - Rover Ash Dissolution Pilot Plant

corrosive conditions anticipated during pilot-plant experimentation. Polypropylene tubing, fittings, and valves were used in processing uncomplexed leachate. The upper end of the vessel was flanged to permit access to the vessel interior. A conical distributor, inside a solid 3-inch diameter spool piece, was welded to the bottom of the polyethylene pipe to form the base of the dissolver. Two sample taps permitted solution removal from the conical section and from a location 18 inches above the bottom of the vessel. A single, vinylidene fluoride-coated thermocouple monitored the solution temperature. A polypropylene-lined reflux condenser was used to condense water vapor, hydrofluoric acid, and fluoboric acid. An air supply line, equipped with a rotameter, entered the vessel at the apex of the conical distributor and permitted a metered addition of sparge air to the dissolver. Heated water, pumped through tubing wrapped around the dissolver, maintained the desired dissolver temperature.

Solids elutriated from the secondary burner were retained in the collection pot directly above the dissolver vessel. Two one-inch ball valves permitted controlled addition of product ash to the dissolver while avoiding pressure fluctuations caused by different conditions in the two systems. Heating tape around the one-inch feed line prevented condensate accumulation.

Borated nitric acid, dilution water, and aluminum nitrate were gravity fed to the dissolver from 4-inch diameter, 2-liter tanks; these solutions were preheated on laboratory hot plates. The corrosive properties of hydrofluoric acid led to the use of a plastic storage vessel, a constant-temperature bath, and peristaltic pump as the pilot-plant reagent supply system.

Process Description

The dissolution materials flowsheet is shown in Table IV. The dissolution process includes feed charging, HNO_3 dissolution, HF dissolution, complexing, and transfer of dissolver effluent to a settling tank. A nominal 200 grams per batch of secondary-burner ash (scaled down from plant equivalent rates shown in Table IV) was charged to the dissolver. With the exception of the first few runs the air sparge was maintained

at 1.2 ft/min superficial velocity.

Nitric acid (8 M) was fed batchwise at the top of the vessel at a sufficiently slow rate to prevent excessive temperatures. Temperatures greater than 80°C generate excessive foam; the maximum required HNO₃ dissolution period was 30 minutes.

Dilution water and concentrated HF were fed sequentially following the HNO₃ dissolution period. The HF concentration at the beginning of the HF dissolution period was 8 M. The HF dissolution period requires 3 to 4 hours to obtain complete dissolution of Nb₃UO₁₀ and 70% dissolution of niobium.

Following the HF dissolution period, the dissolver liquid was sampled, analysed for free fluoride concentration, and complexed with 2.2 M Al(NO₃)₃. After a complexing period requiring about five minutes, the dissolver effluent was slurried by gravity flow to a settling tank for solids removal.

Uranium and niobium throughput data shown in Table IV are based on the anticipated average composition of Rover fuel to be processed. The total moles of nitric and hydrofluoric acid added, however, provide a stoichiometric excess over that required for anticipated "extremes" in dissolver charge composition.

Such a procedure permits the dissolution of secondary burner ash of unknown composition; only the mass of the charge is required to determine the volumes of acid and dilution water required. Aluminum nitrate addition is based on free-fluoride probe titrations of dissolver samples. The final four streams in Table IV indicate the feed adjustments required before transfer to the extraction system.

Experimental Testing and Results

Ten major pilot-plant runs were made to determine flowsheet conditions necessary to obtain greater than 99.8% recovery of uranium, while maintaining stable dissolver solutions. Run conditions and the results of the ten pilot-plant tests are summarized in Table VII. Flowsheet modifications were made during the first seven runs; the final three runs were a part of the Rover process demonstration.

TABLE VII SUMMARY OF RUN CONDITIONS AND RESULTS--ROVER PROCESS DEMONSTRATION

Run No.	Operating Conditions	Uranium charged (gms) ⁽²⁾		Niobium ⁽¹⁾ Charged (g)	Uranium Dissolved, %	Niobium Dissolved, %	Solids Residue (g)	Comments
		U ₃ O ₈	Nb ₃ UO ₁₀					
1	5M HNO ₃ - 15 min. 12M HF - 1 hour. Proc. Temp. - 68°C	88.4	6.0	14.8	99.2	30.4	20.0	Initial Flowsheet Conditions
2	5M HNO ₃ - 30 min. 12M HF - 4 hours. Proc. Temp. - 68°C	95.9	6.5	13.2	99.7	66.5	8.0	Rate Study - Initial Flowsheet
3	8M HNO ₃ - 1 hr. 4.3M HF - 4 hrs Proc. Temp. - 75°C	RUN TERMINATED ----EQUIPMENT PROBLEMS						Add Dilution Water Before HF
4	8M HNO ₃ - 1 hr. 4.3M HF - 4 hrs. Proc. Temp. - 75°C	74.8	22.9	27.9	92.6	22.9	44.0	Repeat of Run -3, Nb, U Recovery Too Low
5	8M HNO ₃ - 1 hr. 8M - 4 hrs. Proc. Temp. - 80°C	76.2	23.3	34.1	95.4	50.1	42.0	Mixing Problems Noted
6	8M HNO ₃ - 1/2 hr. 8M HF - 4 hrs Proc. Temp. - 78°C	82.8	25.4	35.3	99.1	83.5	13.8	New Sparge Design
7	8M HNO ₃ - 1/2 hr. 8M HF - 4 hrs Proc. Temp. - 78°C	100.0	6.1	35.8	99.7	54.1	18.0	Repeat Run 6 Reduced Sampling
8	8M HNO ₃ - 1/2 hr. 8M HF - 3 hrs. Proc. Temp. - 78°C	97.6	6.9	28.3	99.9	65.8	13.6	Rover Demonstration
9	8M HNO ₃ - 1/2 hr. 8M HF - 3 hrs. Proc. Temp. - 78°C	79.6	16.3	58.9	99.8	65.3	28.7	"
10	8M HNO ₃ - 1/2 hr. 8M HF - 3 hrs.	75.1	16.1	67.3	99.8	59.1	39.6	"

1. 200 grams were charged to dissolver in all runs except RL-8 in which 166 grams were charged.
2. Uranium and niobium input data based on output analyses. Figures are the metal content of the ash.

Dissolution Flowsheet and Equipment Development

Run 1 was conducted at the flowsheet conditions developed in glassware studies. Specific operating procedures and conditions for this initial run were:

1. Two hundred grams of secondary-burner ash were charged to the dissolver.
2. 5 M nitric acid, preheated to 75°C, was gravity fed to dissolver.
3. The air sparge was adjusted to a rate equivalent to a superficial velocity of 2.5 ft/min.
4. After a 15-minute nitric acid dissolution, 22 M HF (preheated to 75°C), was pumped into the dissolver.
5. Dilution water was added one hour after the HF addition and a solution sample taken.
6. X-ray fluorescence analyses determined the niobium content of the solution and $\text{Al}(\text{NO}_3)_2$ was added on that basis.
7. The complexed solution was slurried from dissolver to a receiving vessel.

Several problem areas were identified in Run-1. Uranium recovery appeared acceptable; however, only 30% of the niobium dissolved. Also, a higher UO_2F_2 content than had been anticipated was noted in the undiluted solution. Finally, the X-ray fluorescence analytical technique, as developed, was inadequate. The method was time consuming and the error too great for assuring a complexed dissolver solution.

Run-2 was primarily a dissolution rate study for both the uranium and niobium. The nitric leach was extended to 30 minutes and the HF dissolution to four hours; other conditions were the same as those in Run-1. Leachate samples taken throughout both phases of the dissolution indicated the following: (1) U_3O_8 dissolution did not reach completion in 30 minutes, (2) approximately 55% of the uranium was present in solid UO_2F_2 form before dilution water was added, and (3) the UO_2F_2 content in the undiluted leachate reached 350 grams/liter.

The following flowsheet adjustments were made to correct these problems: (1) the nitric acid concentration was increased to 8 M to

increase the U_3O_8 dissolution rate, (2) the solution was diluted prior to HF addition to eliminate UO_2F_2 precipitation, (3) the concentration of HF added was increased to 28.4 M to reduce the dissolver volume required, and (4) three new flowsheets with HF concentrations of 4 M and 8 M were proposed for pilot-plant evaluation. The basis of evaluating lower HF concentrations was evidence that elimination of the UO_2F_2 precipitate would improve acid/solids contact, thereby increasing uranium and niobium dissolution rates.

Run-3 and -4 were essentially identical tests of the 8 M HNO_3 - 4 M HF flowsheet. Run-3 was terminated prematurely because a flaw was discovered in the dissolver wall; however, the nitric acid dissolution was completed before equipment problems developed. Samples showed that U_3O_8 dissolution in 8 M HNO_3 was complete within 30 minutes.

Run-4, a repeat of Run-3, showed inadequate dissolution both of uranium (92.3%) and niobium (22.9%). Formation of the UO_2F_2 precipitate was eliminated by the change in sequence of the dilution step. No solids were observed at any time in the uncomplexed solution. Free-fluoride probe titration of a sample was used successfully to determine the volume of 2.2 M $Al(NO_3)_3$ solution required for complexing. This method is more rapid (~ 15 minutes) and accurate than the x-ray analysis originally proposed.

The inadequate dissolution of niobium obtained with the 4 M HF flowsheet prompted investigation of an 8 M flowsheet in Run-5. One hour was allotted for the 8 M nitric acid dissolution and 4 hours for the HF- HNO_3 dissolution. Only 95.4% of the uranium and 50.1% of the niobium dissolved under these conditions. This poor recovery compared to greater

than the 99.8% U and 75% Nb recovery attained in similar conditions in the laboratory was attributed to poor solids-liquid contact. The air sparge rate had been decreased to ~ 1.2 scfm/ft² relative to a much higher rate used in Run-1 to reduce the sparged leachate volume. Decreased turbulence permitted the accumulation of solids in regions at the bottom of the dissolver.

A conical distributor section was added at the base of the dissolver to increase solids mixing, and the conditions of Run-5 were repeated in Run-6. Although apparent uranium recovery (99.1%) did not meet the process requirement, the six samples taken during the run diverted enough material to account for this small deficiency (actual uranium recovery was believed to exceed 99.8%). Uranium and niobium dissolution data obtained in Run-6 are shown in Figure 5.

Run-7 was a repeat of these conditions to determine the effect of sampling; a single solution sample was taken during the run. Results showed a uranium recovery of 99.7%. However, niobium dissolution was lower (54.1%) than in Run-6.

Although the disparity in niobium dissolution rates determined in Runs-6 and -7 was unresolved, the 8 M HNO₃ - 8 M HF flowsheet was adopted for use in the Rover product-train demonstration run. Results from the demonstration run indicated that the Run-7 niobium analysis was in error.

Dissolution Flowsheet Demonstration

The final three runs in the dissolution pilot-plant, Runs-8,-9, and -10, were conducted consecutively as part of the Rover product-train demonstration. Three batches of primary burner product ash, selected on the basis of wide variation in composition, were charged to the secondary burner. Immediately after elutriation, a weighed batch of essentially carbon-free ash was charged to the dissolver. Despite the reduced run time (3½ hours for each batch) and the wide variation of uranium content in each batch, uranium dissolution was $\sim 99.8\%$. Niobium dissolution corresponded closely to data obtained in Run-6. Niobium dissolved from each batch was in the 59 to 65% range.

Figure 5. - Concentration of U and Nb in Dissolver Solution during Sequential HNO₃-HF Dissolution Cycle

During the dissolution process demonstration, the performance of each piece of pilot-plant equipment was evaluated. Overall operation of the pilot plant was satisfactory, i.e., all experimental objectives were realized. However, some equipment and procedural modifications would improve process operability and efficiency. Specific performance observations of pilot-plant equipment are included in the following paragraphs. More detailed discussions of settling tank and centrifuge performance are given in Section IV.

Charging product ash to the dissolver from the collection pot through two ball valves requires vibration to assure that solids bridging does not occur. Surfaces on which vapors can condense must be heated to $\sim 100^{\circ}\text{C}$; failure to do so in one run resulted in solids caking on all wetted surfaces. Addition of an air purge immediately below the lower charging valve would further assure a moisture-free charging system.

Dissolver vessel operations were generally satisfactory. The conical air-spargе distributor promoted solids-liquid mixing over a wide range of solids loadings. Solids which adhered to the vessel wall during charging were rapidly washed into the solution by condensation. Condensation takes place at the internal wall of the dissolver during dissolution. However, initial contact between heated nitric acid and product ash resulted in vigorous foaming, which could be a problem in scaled-up equipment. Step-wise addition of the nitric acid or addition of cold or more dilute acid should eliminate foaming.

The pilot-plant reflux condenser did not provide adequate contact to remove all HF vapors from the off-gas stream; a gradual reduction in dissolver fluoride content was noted. No depletion of the boron content was noted, however, indicating little or no escape of fluoboric acid vapors from the dissolver. Plastic packing rings in the condenser might be required in plant-scale equipment.

The dissolver slurry was removed by maintaining the normal air sparge rate while allowing the dissolver contents to drain into the settling tank. With the exception of holdup in any piping penetration of the vessel, solids removal was satisfactory.

Proposed Plant-Scale Dissolution Process

Based on pilot-plant results, the 8 M HNO_3 - 8 M HF flowsheet and the previously described dissolver vessel design are recommended for the proposed plant-scale process. All process requirements were met in the pilot-plant dissolution process, and the proposed design is readily adaptable to current plant practice. The operating sequence and conditions which were developed are as follows:

1. Determine the mass of product ash to be charged to the dissolver.
2. From the mass of the charge, calculate the quantity of nitric acid, dilution water, and hydrofluoric acid to be added.
(proportional to mass charged in average flowsheet--Table IV).
3. Charge ash to dissolver and slowly add preheated 8 M nitric acid.
4. Start air sparge (1.2 scfm/ft²).
5. After 30 minutes, add preheated dilution water.
6. Add preheated 8 M hydrofluoric acid.
7. Following a dissolution period based on desired niobium dissolution, sample dissolver solution.
8. Determine quantity of 2.2 M $\text{Al}(\text{NO}_3)_3$ required for complexing by using the free-fluoride probe titration.
9. Add $\text{Al}(\text{NO}_3)_3$, allowing five minutes for adequate mixing.
10. Slurry complexed solution to settling tank.

An upper limit of 27 kilograms per batch was assumed for the mass of product ash to be charged to the plant dissolver; the maximum volume of complexed solution would be 400 liters. This is based on a zero niobium-maximum uranium charge which requires a maximum volume of 2.2 M $\text{Al}(\text{NO}_3)_3$ for complexing. An additional 150 liters for de-entrainment and volume occupied by sparged liquid results in a total dissolver volume of 550 liters. Dimensions of the cylindrical vessel will be determined by criticality safety considerations.

The highly corrosive conditions in the dissolver preclude the use of even high nickel-chrome alloys. A plastic-coated or lined stainless steel vessel will be necessary to prevent corrosion failure. The base of the vessel should have a conical distributor section to eliminate solids accumulation in stagnant regions.

Conclusions and Recommendations

The following conclusions are based on results from the pilot-plant development studies and demonstration runs:

1. The secondary-burner product ash must be weighed prior to charging; ash can readily be gravity-fed to the dissolver, if all pipe surfaces are dry.
2. Adequate mixing of the product ash with the acids is obtained with an air sparge fed into a conical section at the base of the dissolver.
3. Operation of the pilot-plant dissolver at 80°C with the 8 M HNO_3 - 8 M HF flowsheet provides:
 - a. 99.8% recovery of uranium contained in secondary-burner ash within 3 to 4 hours.
 - b. 60% dissolution of the niobium in 3 hours of combined HF- HNO_3 dissolution time.
4. Slurry of the dissolver product from the dissolver can be accomplished by maintaining the 1.2 scfm/ft² air sparge rate and permitting the solution to drain by gravity from the vessel.
5. The complexed dissolver product is a stable solution.

Recommendations for the proposed plant-scale dissolver are:

1. Product ash should be gravity-fed to the dissolver. A vibrator attached to the feed bin and a gas purge will eliminate solids-bridging problems
2. All surfaces in the product-ash feed system must be kept dry by maintaining the surface temperatures above 100°C while providing an air purge.
3. The dissolver vessel must be resistant to the highly corrosive dissolver solutions. Plastic coating of the interior surface appears to be a feasible approach.
4. If consistent with future criticality calculations and other layout considerations, the dissolver vessel should be cylindrical, 18 inches in diameter, and 14 feet in height. A conical section at the base will help assure adequate solids-liquid contact when used in conjunction with an air sparge system.
5. An effective air sparge design is necessary to obtain the desired dissolution rate and to slurry solids from the dissolver.

IV. LIQUID-SOLIDS SEPARATION IN DISSOLVER PRODUCT

The effluent from the Rover-ash dissolver contains significant quantities of undissolved solids (mainly Nb_2O_5) which must be separated from the uranium bearing solution, washed of occluded uranium, and prepared for disposal.

Process Requirements

Process requirements for the Rover plant liquid-solids separation system are:

1. The solids loading of the extraction column feed cannot contain a significant amount of solids greater than 10 microns in effective diameter.
2. The total solids sent to the plant PEW system must be minimal, since the system is not designed to handle gross quantities of solids.
3. The uranium content of the solids must be compatible with the requirement for greater than 99.5% uranium recovery from the Rover fuel.

To satisfy these requirements, a liquid-solids separation system consisting of a settler-washer, solids collection tank, and a centrifuge is recommended. Specific process requirements for each component of the liquid-solids separation system follow.

1. Settler-Washer

The settler-washer:

- (a) Must remove greater than 90% of the undissolved solids from the dissolver effluent.
- (b) Must contain facilities for washing uranium from undissolved solids.
- (c) Solids-free solution must be transferable from the settler-washer to the centrifuge.
- (d) Washed solids must be slurried to solids collection tanks.
- (e) Solution residence time must not exceed four hours to avoid precipitation problems and limiting plant throughput.

(f) Must include sufficient volume to contain the maximum dissolver charge.

(g) Must be critically safe.

2. Solids Collection Tanks

A large volume (25 to 75 ft³) of undissolved solids will be collected during the Rover campaign. Containers for the solids must meet the following criteria:

(a) At least 75 ft³ of storage capacity should be provided for undissolved solids.

(b) Bulk solids from the settler-washer must be readily separable from the slurry.

(c) Solids must be removable from the container for possible reprocessing.

(d) Simple, safe removal of the tanks from the processing cell to a permanent storage area must be possible.

(e) Containers must provide reliable long-term storage.

3. Centrifuge

The centrifuge must have the following capabilities:

(a) Must remove undissolved solids larger than 10 microns in diameter from the dissolver effluent.

(b) Accumulated solids in the centrifuge must be washed free of occluded uranium.

(c) Accumulated solids in the centrifuge must be readily removable from the centrifuge bowl.

Equipment and Process Description of Pilot-Plant Solids-Liquid Separation System

The pilot-plant equipment used to develop a solids-liquid separation system consisted of a settling tank, simulated plant centrifuge, and product receivers. The settling tank was a quartz container made from 4-inch glass pipe, 14" high, and large enough to contain one batch of complexed dissolver solution. The centrifuge was of the bowl type (radius = 6.3 cm) having a hold-up volume of 350 ml, but it did not have perforated baffles.

During the pilot-plant scale testing, complexed dissolver solution was slurried by gravity from the pilot-plant dissolver into a polypropylene bottle and then immediately transferred to the settling tank. After a settling time of 30 minutes, the contents were sampled (above the heel) and drained into the centrifuge. After draining, the heel was vacuumed through 12 feet of 0.25 in. tubing and slurried to another container for filtration, washing, weighing, and sampling. This procedure was repeated for each batch.

The bowl-type centrifuge was operated at a force of 1000 g to simulate the centrifugal forces obtainable in the existing ICPP plant centrifuge. The flow rate to the centrifuge was about 180 ml/min, corresponding to a mean residence time of about 2 minutes.

The centrifuge effluent was collected in a 2-liter polypropylene bottle and subsequently filtered through millipore filters (pore size 0.45 μ). The contents of the centrifuge bowl was emptied at the end of each run into a glass beaker and was filtered and washed several times. The filter cake was then dried, weighed, and sampled.

Discussion and Results

The solids loading of the settling tank effluent in the pilot-plant runs averaged 1.7 g/liter corresponding to about 95% solids removal in 30 minutes (Table VIII). Since a settling time as great as four hours might be acceptable, the process requirement of 90% solids removal using a settler-wash vessel can easily be met.

Chemical analysis of these solids (Table VIII) shows that the solids in the settling tank were 68.1% Nb and 0.6% U. This corresponds to 97.2% Nb₂O₅ and 0.7% U₃O₈. (No Al analyses were made, but it is assumed that the remaining 2.1% is Al₂O₃.) In terms of the total uranium flow (as undissolved solids) from the dissolver, 81% remained in the settling tanks.

The pilot-plant centrifuge bowl did not have internal baffles as does the ICPP plant-scale centrifuge. This is a serious limitation in simulating the plant centrifuge, but does represent a "worst case" situation. The pilot-plant centrifuge removed an average of 91% of the solids from the settling tank effluent stream. The solids loading of the centrifuge effluent averaged 0.05 g/l. Thus, the centrifuge

effluent stream should cause no solids settling problems in the existing plant extraction columns. Before the installation of the plant centrifuge, the solids loading of the feed streams to the extraction columns was as high as 0.05 g/ℓ

TABLE VIII
CONCENTRATION AND COMPOSITION OF SOLIDS DURING
SOLIDS-LIQUID SEPARATION

	g/ℓ	% of Total (Ave.)	Wt% U	Wt% Nb
Settling Tank Effluent	0.3 - 3.0	4.4	0.9 - 4.8	57.5 - 60.3
Settling Tank Bottoms (gm/ℓ input)	7 - 21	94.8	0.5 - 0.7	66.1 - 69
Centrifuge Effluent	0.03 - 0.07	0.4	1.4 - 16.4	20.7 - 69

Proposed Plant-Scale Process

Complexed dissolver solution could be slurried into the settler-washer vessel and, after two-to-four hours settling time, the supernate (liquid effluent) pumped to the existing plant centrifuge. Solids remaining in the vessel could be washed two or three times with a small volume of water, while the solution is sparged by air. The settler-washer vessel should have a 60° conical bottom section.

Solids, after washing, could be slurried from the settler-washer vessel to solids collection vessels connected in series. Facilities for sampling the slurry could be connected to the collection tank drain line so the efficiency of washing could be assessed. Essentially, solids-free water would overflow from the last vessel and be piped to the plant waste system. Flanged vessel taps could enable removal of the solids, if the necessity arises, for reprocessing or drying of the solids. Because of the anticipated radiation level of the solids, it may be necessary to shield the vessels during transfer to final storage.

Conclusions

The liquid-solids separation system recommended for the Rover plant-scale system includes a settler-washer, solids collection vessels, and

the existing ICPP plant-scale centrifuge. The settler-washer would be included in the process to remove the bulk of the undissolved solids from the dissolver effluent. By installing a settler-washer, the following flexibility is realized: (1) about 95% of the solids would be removed in 30 min., (2) the process would not depend upon the plant centrifuge, (3) the man-hours required for emptying the centrifuge would be reduced from approximately 200 to 15, (4) the undissolved solids from the entire campaign could be contained in collection vessels to permit further uranium recovery from the solids as required. The existing plant centrifuge has adequate capacity for handling the settler-washer liquid effluent.

V. RELATED PROCESS DEVELOPMENT STUDIES

The related process development study areas include (1) startup and supplemental heating of the primary and secondary burners, (2) unique sampling, analytical, and instrumentation requirements, (3) solids transfer demonstration, (4) Nb accumulation in the primary burner, and (5) charging combustible containers to the primary burner.

1. STARTUP AND SUPPLEMENTAL BURNER HEAT

Provisions for startup and supplemental heating of the Rover plant-scale burners are required to initiate combustion and to maintain the burners at a reasonably constant operating temperature during fuel processing. The heating method must be totally reliable, be compatible with direct maintenance, and provide heatup in a reasonable time period without exceeding allowable surface temperatures.

Startup Transients

Computed bed-temperature-time curves for the plant-scale primary and secondary burners are shown in Figures 6 and 7, respectively. The important assumptions used to derive the heat balance equations are:

1. The installed heater capacity in the primary and secondary burners is 120 and 40 kW, respectively. The heaters are 1/2" dia. sheathed cylinders positioned vertically every two inches around the vessel wall in the cooling shroud opposite the expanded fluidized bed. The rated watt-density of the heaters is 25 watts/in.².
2. Each burner is surrounded by 3" thick magnesia insulation. Heat loss is based on inside and outside temperatures of 1600°F and 80°F, respectively.
3. The fluidizing air flowrate is adjusted to maintain constant superficial velocity in the fluid bed. The fluidizing air is heated at the same rate as the bed to 1000°F, the maximum fluidizing air inlet temperature.

Figure 6. - Effect of Power Input on Startup Time for Rover Primary Burner

Figure 7. - Effect of Power Input on Startup Time for Rover Secondary Burner

4. The bed temperature equals the vessel temperature in each burner, except that the filter section in the secondary burner is cooled by air.

No attempt was made to compute the individual resistances and temperature drops for heat transfer from the electrical heaters to the bed. However, experience with a similar heater configuration in the ICPP Graphite Fuels Pilot Plant has shown that the heaters will operate reliably without danger of burnout at the fractional (1/8-1/2) power levels assumed for calculation of the temperature transients. In actual practice, power levels would be reduced as required during startup to prevent the heater internal temperature from exceeding an operating limit of approximately 1600°F. Since vessel integrity is also of prime consideration, vessel wall temperatures were computed at a bed temperature of 1400°F for each power level and for surface-to-bed heat transfer coefficients of 25 and 50 Btu/hr-ft²°F. The wall temperatures shown in Table IX must be less than the limit specified for the materials of construction.

Supplemental Heating Rates

The rate-of-change of bed temperature with various power levels at an initial temperature of 1400°F is given in Table X. These rates are adequate for maintaining proper temperature levels during periods of declining combustion rates in both the primary and secondary burners. A sudden drop of about 200°F in secondary bed temperature is predicted while charging cold primary ash to the secondary bed. If the temperature falls below the ignition point of 1148°F, the supplemental heating rates indicate that temperature recovery will be rapid.

Process Heat Removal

Heat removal rates were estimated for air flowing through the cooling shrouds of the primary and secondary burners at a nominally selected entrance velocity of 100 ft/sec. The estimated overall heat transfer coefficient at this velocity is 5 Btu/hr-ft²-°F; the cooling capacity of the primary burner at this condition is 3.1×10^5 Btu/hr. This cooling capacity is adequate for semi-continuous combustion of Rover fuel at the present plant flowsheet rate.

TABLE IX

EFFECT OF OPERATING POWER LEVEL AND HEAT TRANSFER
COEFFICIENT ON VESSEL WALL TEMPERATURE
(Constant 1400°F Bed Temperature)

	Wall Temperature, °F		
Primary Burner	(P = 15 kW)	(P = 30 kW)	(P = 60 kW)
U = 25	1425	1455	1529
U = 50	1412	1427	1465
Secondary Burner	(P = 5 kW)	(P = 10 kW)	(P = 20 kW)
U = 25	1448	1477	1574
U = 50	1424	1438	1487

TABLE X

EFFECT OF OPERATING-POWER LEVEL ON
RATE OF CHANGE OF BED TEMPERATURE
(Initial 1400°F Bed Temperature)

	Rate of Change of Bed Temperature, °F/hr.			
Primary Burner	(P = 0 kW)	(P = 15 kW)	(P = 30 kW)	(P = 60 kW)
	-44.	+31	+107	+257
Secondary Burner	(P = 0 kW)	(P = 5 kW)	(P = 10 kW)	(P = 20 kW)
	-97	+67	+231	+559

The cooling capacity of the secondary burner, also based on an overall coefficient of $5 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F}$, is only $9.3 \times 10^4 \text{ Btu/hr}$; batch combustion using 100% O_2 as the fluidizing medium could release up to $2.3 \times 10^5 \text{ Btu/hr}$. Therefore, cooling air velocities greater than 100 ft/sec or dilution of the O_2 with air will be required to prevent temperature excursions in the secondary burner.

2. UNIQUE ANALYTICAL AND INSTRUMENTATION REQUIREMENTS

An evaluation of the unique instrumentation and analytical requirements for the proposed plant-scale process follows. Accountability of uranium is the primary reason for the majority of the proposed samples. Other samples can be used to determine the extent of ash dissolution, complexing requirements, and operating efficiencies.

Primary and Secondary Burner Bed Samples

The primary and secondary burner beds should be sampled and analyzed for uranium and niobium by an X-ray fluorescence technique. These samples would provide uranium inventory data as well as information on uranium and niobium buildup in the bed.

Weight of Secondary Burner Ash

The amount of product charged to the dissolver must be known within $\pm 5\%$; this can be accomplished by means of weigh-hoppers (using loadcells or equivalent) used as charging pots.

Dissolver Solution Samples

A sample can be taken from the dissolver at the end of the dissolution step to determine fluoride complexing requirements. Aluminum nitrate can be used to complex the fluoride, and the amount of aluminum nitrate required can be determined by a fluoride electrode and a recording potentiometer.

Fluoride Probe Complexing

A fluoride electrode can measure the potential due to "free fluoride", i.e., that fluoride which is not complexed. Because of the complexity of the dissolver solution matrix, the "free fluoride" cannot be measured directly by existing methods. Therefore, the most practical method of determining

the amount of complexer to be added to the dissolver is by titrating a sample of dissolver solution with aluminum nitrate to a potentiometric end point. The amount of aluminum nitrate required to complex the dissolver solution can then be calculated. Overcomplexing results in a Nb_2O_5 precipitate, while undercomplexing usually results in an $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ precipitate. The fluoride electrode eliminates any guesswork in complexing this five-variable system.

Dissolver Solids Analysis and Extent of Dissolution

The undissolved solids loading in the dissolver can be determined from the same dissolver sample taken for complexing; the uranium and niobium content of the solids can be determined by X-ray fluorescence. The supernate from the dissolver sample can also be analyzed for uranium and niobium by the X-ray fluorescence technique. Solids and liquid analyses of dissolver solutions provide information relative to: (1) extent of dissolution of uranium and niobium, (2) uranium content of the solids, (3) uranium accountability, (4) separation of solids in the settling tank, and (5) burning and elutriation efficiencies of the burners.

3. SOLIDS TRANSFER DEMONSTRATION

Due to the lack of vertical clearance in the mechanical handling cave proposed for the Rover plant facilities at ICPP and the possibility of locating the secondary burner in that cave (for maintenance and operational reasons), it might be necessary to pneumatically transfer ash from the primary burner collection pot to the secondary burner charging pot; this operation requires air lifting the ash. Solids flow in such systems is influenced by three primary variables: (1) pressure differential, (2) vibration, and (3) elapsed time of transfer. The extent to which these variables influence the transfer of primary-burner ash was studied in a simulated plant system.

Experimental Model

A series of experiments was conducted to demonstrate the feasibility of transferring primary ash by air jet and to identify solids transfer problems that may be unique to the specific primary burner ash. The

experimental model selected for the demonstration is shown in Figure 8. The primary components of the model were a simulated primary collection vessel, an air jet, and a solids collection pot. The primary collection pot was isolated by ball valves, was equipped with a pneumatic vibrator, and had provisions for pneumatic pressurizing. The air jet orifice was 5/16" diameter, and the supply jet was located 0.221" upstream of the venturi orifice. The collection pot contained a sintered metal filter and blowback equipment. A vertical rise was incorporated into the piping and the flow path was purposely designed to be more tortuous than that anticipated in the plant-scale system.

Experimental Procedure

The experimental procedure for operating the equipment was to maintain the jet air flow rate at the normal rate used through the collection pot filter (39.9 scfh) and activate the blowback system at all times. The desired pressure differential was established by pressurizing the simulated collection vessel, and the vibrator was activated as desired. The bottom ball valve associated with the simulated collection vessel was opened for the desired time interval. At the end of each interval, the receiving vessel was drained to determine the amount of solids transferred.

Experimental Results

The results of the experimental testing are summarized in Table XI. For the desired mode of operation, the weight of solids transferred was determined after one minute, after a second minute, and after a third minute. Residual solids were then drained from the feed vessel. Testing was also conducted continuously for two and three minutes with subsequent draining of residual solids from the feed pot.

In addition to the tests corresponding to the tabulated results shown in Table XI, a packing test was made in which the vibrator alone was operated for one minute followed by two minutes of air jet operation. Only 23.7% of the solids was collected during this time.

Conclusions and Recommendations

Results indicate the following:

Figure 8. - Schematic Diagram of Solids Transfer Demonstration Equipment

TABLE XI

EFFECT OF AIR JET AND VIBRATOR ON SOLIDS TRANSFER
(Expressed as percentage of solids transferrable)

	Test I				Test II	Test III
	First Minute	Second Minute	Third Minute	Drain	Two Minutes	Three Minutes
Operation Jet Only ¹	41.7	41.6	13.1	3.6	80.3	93.0
	40.2	42.6	11.2	3.8	75.2	94.4
						93.9
Jet and Vibrator ¹	53.6	45.4	1.0	0	90.6	99.0
	41.5	43.5	13.4	1.7	67.5	97.3
	38.7	38.9	21.8	0.6		98.2
Jet Only ²	88.7	3.1	1.4	6.8		
	88.5	3.9	0.4	7.0		
Jet and Vibrator ²	89.7	8.1	1.3	0.8		
Jet and Pressurized Vessel ²	89.1	2.6	0.9	7.4		

¹ Approximately 200 g solids charged.

² Approximately 80 g solids charged.

- (1) An air jet alone is very effective when more than 20% of the material remains in the solids charging vessel, if only minimal solids packing has occurred.
- (2) Pressurizing the solids charging vessel has no noticeable effect on the transfer when used in conjunction with the air jet.
- (3) A vibrator operating in conjunction with an air jet gives the most complete solids transfer, but the effect of the vibrator is not significant until approximately 80% of the solids have been transferred.
- (4) A vibrator can have a detrimental effect when it is not operated concurrently with the jet or an air purge.

In general, the model used was very effective in transferring solids. The jet provided a particle entrainment medium and prevented solids bridging, and the vibrator allowed reasonably complete drainage of the simulated collection vessel. Air purges or impulses appear necessary to break up solids bridges.

4. Nb ACCUMULATION IN PRIMARY BURNER

Tests conducted using the Graphite Fuels Pilot Plant have shown that the niobium inventory in the fluid-bed burner increases during combustion of fuel elements containing niobium. Niobium accumulation in the Rover plant-scale burner at rates corresponding to those experienced in the pilot plant would result in a 40-70% increase in bed weight for a projected 100-day Rover-fuels campaign.

The niobium in the burner beds exists primarily as niobium oxide particles (Nb_2O_5), which are too large to elutriate rapidly from the burner. Jet grinders are effective in decreasing the size of Nb_2O_5 particles; however, the jet grinder capacity used in actual tests was insufficient to prevent niobium accumulation in the bed.

The following are possible adverse consequences of excess niobium accumulation in the burner bed:

1. Bed-level increase to the point where the decreased freeboard height results in excessive alumina entrained into the overhead product collection pot.
2. Increased bed weight interferes with fluidization and hence, in-bed heat transfer, thereby increasing the possibility of damage to the burner.

SUMMARY OF NIOBIUM BUILDUP IN PILOT-PLANT PRIMARY BURNER
(Runs A-5 through A-11)

Run A-5

The run was started with a fresh bed of alumina; charging rate of fuel was based on 16 kg C/hr-ft^2 bed cross-sectional area; jet grinders were not employed. Niobium accumulated at a steady rate during the 96-hour run to 3% of the final bed weight.

Run A-6

Fresh alumina was used and charging rate was 16 kg C/hr-ft^2 ; jet grinders were not used. Niobium reached 16% of the bed weight at the end of a 240-hour run. Microscopic examination showed Nb_2O_5 exists as flakes in burner and did not coat inert bed material.

Run A-7

The run was started with final bed from A-6, and the charging rate ranged from 15 to 33 kg C/hr-ft^2 ; jet grinders were not used. Analytical data indicated that niobium concentration remained stable at 7-8%, based on a large number of bed sample analyses. The discrepancy between these analytical results and earlier results is assumed to be due to sampling errors.

Runs A-8 and A-9

Fresh alumina was used and the charging rate was 16 kg C/hr-ft^2 ; four jet grinders with 100 psig air were used. Niobium concentration reached 3.2% at the end of 186 hours. Jet grinders resulted in a slower rate of niobium accumulation than observed in Run A-6.

Run A-10

The run was started with the final bed from A-9 and the charging rate was 16 kg C/hr-ft²; four jet grinders with 100 psig air or oxygen were used. Niobium concentration increased from 6% to 11% during the 240-hour run.

Run A-11

The run was started with the final bed from A-10; other conditions were the same as in A-10, except oxygen only was used in the jet grinders. Niobium concentration increased from 10% to 13% during the 104-hour run.

Recommendations

The following actions are recommended for limiting and monitoring Nb buildup in the primary plant-scale burner:

1. Larger jets and as much as 25% more jet grinder capacity.
2. Bed samples should be taken periodically to determine level of niobium buildup.
3. If freeboard is reduced significantly by an increase in bed height (as measured by bed pressure drop), the excess bed material should be drained from the vessel.
4. If excessive bed temperature spreads occur, the entire bed should be replaced to prevent potential equipment damage. The used bed should be handled as previously described.

5. CHARGING COMBUSTIBLE CONTAINERS TO THE PRIMARY BURNER

More than 25% of the total graphite fuel inventory that will be burned in the Rover head-end process at the ICPP could be in the form of broken and/or severed fuel elements. Packaging these fuel pieces into combustible containers will simplify the burner-charging procedure and reduce the probability of plugging the primary-burner charging tube with irregular fuel pieces. The combustible containers will also provide a back-up means for charging whole fuel elements if excessive plugging of the charging tube occurs.

Process Requirements

Combustible containers must meet the following requirements:

1. Capable of being handled remotely and charged into the primary bed without plugging the charging tube or breaking.
2. Rapidly oxidize and disintegrate at burner temperature without interfering significantly with the normal combustion process for graphite fuel elements.
3. Be readily available at low cost.

Process interactions that must be minimized or avoided include production of excessive ash, sintering of bed material, reduction of combustion efficiency, formation of "tacky" compounds within the bed, alteration of the overhead product (that would affect succeeding process steps), and evolution of explosive combustion products. Also, safety with respect to criticality must be assured.

Types of Combustible Containers Considered

Types of combustible containers which have been considered include those made of aluminum, plastic, and cardboard. Tubular aluminum shipping containers for Rover fuel elements are available; however, pilot-plant tests showed that aluminum does not completely oxidize and disintegrate in a fluid-bed burner. Plastics cannot be used because the temperature in the charging tube exceeds the melting or softening temperature of most plastics.

Cardboard containers, the most promising material considered to date, are available at low cost (several cents per container) and in a variety of sizes suitable for packaging Rover fuel pieces. Tests with cardboard containers in Run A-11 of the Graphite Fuels Pilot Plant are described.

Tests with Combustible Containers

The combustible containers used in Run A-11 were cardboard cylinders 60-in. long by 1-in. O.D. having a 0.07-in. wall thickness and weighing 140 grams. Eleven combustible containers, each containing a whole or slightly damaged Rover fuel rod, were charged to the pilot-plant burner during a 4.6-hour period near the end of the run. Since each container

added only 20% to the weight of the charge, the actual fuel charging rate was not altered for the test.

Charging was smooth except for a single case of fuel dropping through the bottom of a container during the charging procedure. The containers were rapidly oxidized as indicated by a surge in CO and CO₂ concentrations in the off-gas. Normal levels of CO and CO₂ are roughly 2% and 40%, respectively; peak concentrations of approximately 9.5% and 80%, respectively, were attained shortly after each charge. The off-gas analyses showed no unusual components, and the overhead product did not contain any significant quantity of water. No other deviations from normal process conditions were observed.

Combustible Containers in the Rover Plant Burner

Based on the results of the pilot-plant studies, the most important factor to consider in using combustible containers in the plant-scale burner is container integrity.

The containers used in pilot-plant work were made from helically wound strips of cardboard in a manner similar to the cardboard rolls for ordinary paper towels. Thus, care would have to be taken to avoid rough handling of the tubes; otherwise, the cardboard would partially unwind and not slide smoothly down the charging tube. One end of the container must bear the entire weight of the fuel when the container is in a vertical position; therefore, that end would need to be securely fastened to the walls of the container to prevent fuel from dropping through, such as occurred in the pilot-plant tests. The water content of the overhead product ash after charging combustible containers was negligible.

Conclusions and Recommendations

Cardboard containers can meet all process requirements for charging broken and/or whole graphite fuel elements to the Rover plant burner. However, pilot-plant tests have shown that care must be taken to maintain the physical integrity of the containers.

The temperature of the primary collection pot should be maintained greater than 100°C to ensure that water does not condense from the off-gas and plug the filters in the off-gas system during burning of cardboard containers.

VI. CONCLUSIONS

Pilot-plant results and calculations show that 99.8% of the uranium in primary burner ash can be recovered. Specific conclusions regarding the process are:

1. The carbon content of primary burner ash can be reduced to less than 2% by weight in a secondary burner while maintaining a corresponding Al_2O_3 content of less than 1% of the total ash.
2. As much as 99.8% uranium and 70% of the Nb can be dissolved in a 3.5-hour dissolution period using a sequential 8 M HNO_3 - 8 M HF dissolution scheme.
3. The dissolver solution can be accurately complexed with $\text{Al}(\text{NO}_3)_3$, and the dissolver solutions are stable.
4. Greater than 90% of the undissolved solids can be separated in a settling tank.
5. Due to the corrosiveness of the HNO_3 - HF solutions, a plastic lining will be required in the dissolver vessel.
6. Gas purges and vibrators are necessary to insure reliable dry solids transfer.

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