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PROCESS CHEMISTRY FOR BURNER PRODUCT FROM
GRAPHITE FUELS CONTAINING NIOBIUM

BY

B.E. Paige

T.L. Evans

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IDAHO NUCLEAR CORPORATION

NATIONAL REACTOR TESTING STATION
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B. E. Paige

T. L. Evans

IDAHO NUCLEAR CORPORATION

A Jointly Owned Subsidiary of

AEROJET GENERAL CORPORATION
ALLIED CHEMICAL CORPORATION
PHILLIPS PETROLEUM COMPANY

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ABSTRACT

A burn-leach process is being developed for reprocessing Rover rocket fuels at the Idaho Chemical Processing Plant. Data are reported for an aqueous process for recovering uranium from the HNO_3 -soluble oxide in the burner product and also from the HNO_3 -insoluble uranium, $\text{Nb}_3\text{UO}_{10}$, which forms during combustion. Dissolution rates of $\text{Nb}_3\text{UO}_{10}$ and of Nb_2O_5 from overhead product increased with increasing fluoride concentration both for various concentrations of hydrofluoric acid and for mixtures of hydrofluoric-nitric acid. Solubility of uranium in the dissolver product and the species precipitated are discussed. A stable region for Nb-Al-F solutions is defined. The corrosion of stainless steel is evaluated with respect to the degree of complexing of the fluoride by niobium. A dilute uranium dissolver product with minimum fluoride-to-niobium mole ratio, completely complexed at 0.4 M aluminum or less, is the best extraction feed from the standpoint of stability and corrosion of extraction equipment.

SUMMARY

A burn-leach process is being developed for reprocessing Rover rocket fuels. Leaching with nitric acid satisfactorily dissolves uranium oxide elutriated in overhead product from the burner; however, some types of fuel produce a non-leachable uranium, identified as $\text{Nb}_3\text{UO}_{10}$, which requires hydrofluoric acid for dissolution. From the standpoint of dissolution rates of $\text{Nb}_3\text{UO}_{10}$ and Nb_2O_5 , several mixtures of hydrofluoric-nitric acid and different concentrations of hydrofluoric acid were acceptable. Dissolution rates increase with increasing hydrofluoric acid concentration, but high fluoride-to-niobium mole ratios in the dissolver product result in unstable solutions when complexed with aluminum. At hydrofluoric acid concentrations greater than 8 M, the solubility of uranium in niobium dissolver product ranges from 20 to 44 g/l. A minimum of 0.1 M nitric acid is necessary in the dissolvent to prevent the formation of UF_4 and to assure precipitation of only UO_2F_2 from saturated dissolver product.

Within a limited range of compositions, fluoride in stable solutions can be adequately complexed with additional aluminum to prevent corrosion in stainless steel extraction equipment; addition of other fluoride complexers to these stable solutions causes formation of precipitates. Because of the change in both corrosivity and stability created by extraction of uranium, complexed fluoride solutions with greater than 0.25 M uranium can not be used as extraction feed, and a dilute extraction flowsheet, similar to current flowsheets for zirconium fuel, must be used.

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I. INTRODUCTION

A burn-leach process is being developed for the reprocessing of Rover rocket fuel at the Idaho Chemical Processing Plant (ICPP). The fuel is combusted in a fluidized-bed burner operated at 700° to 800°C^[1] to remove the bulk of the graphite, and the uranium oxide product is collected from the overhead gases together with any inert solids which are elutriated from the burner. In addition to the uranium, this overhead product contains niobium oxide, unburned carbon, and small quantities of the inert alumina bed material. These solids must be processed to produce a solution from which uranium can be recovered by the existing extraction facilities at ICPP. Previous schemes for reprocessing of the overhead product^[2] have used only a nitric acid leaching to dissolve U_3O_8 from the other solids; some have also included extraction of a concentrated feed directly in the second-cycle hexone extraction system^[3]. During recent operation of the fluidized-bed burner in the pilot plant^[4], significant amounts of HNO_3 -insoluble uranium were formed when different types of fuel were combusted. This portion of uranium is not recovered by a simple nitric acid leach process and could constitute a loss from the process unless otherwise dissolved. The purpose of this study was to develop a process for near total recovery of uranium when significant quantities of HNO_3 -insoluble uranium are present in the overhead product from the graphite burner.

Hydrofluoric acid is required to dissolve the uranium which is insoluble in nitric acid. Rates of dissolution were determined at several hydrofluoric acid concentrations and in mixtures of hydrofluoric and nitric acids to provide basic data for design of the dissolvers. The solubility of the uranium in the dissolver product was examined during these dissolution studies. During the reprocessing of zirconium-fluoride solutions at ICPP, aluminum is added to complex the excess fluoride which is not complexed by zirconium in order to prevent corrosion of stainless steel extraction equipment. Niobium-fluoride solutions complexed with aluminum nitrate were evaluated with respect to degree of complexing of the fluoride and corrosion rates. In the processing

of zirconium-fluoride solutions, stability often dictates the composition of process solutions. In this study, the stabilities of niobium-aluminum-fluoride (Nb-Al-F) solutions were examined, and a concentration range of stable solutions was defined.

Current studies were made using three different reagents for dissolution of the HNO_3 -insoluble uranium. Selection of reagents was based on flowsheets which used different modes of operation with types of equipment which required different reagents and concentrations in process streams. Two methods of separating solids from the burner off-gas were considered. Separation by a nitric acid scrub requires large volumes of scrub solution resulting in dilute uranium solutions; a flowsheet using 6 M HNO_3 -2 M HF was selected for this mode of separation. Dry separation of solids from off-gas resulted in a concentrated dissolver product using either of two modes of dissolution. In the one-step mode, all uranium is dissolved during the dissolution, and the dissolvent contains nitric acid for the dissolution of U_3O_8 as well as hydrofluoric acid for dissolution of the HNO_3 -insoluble uranium; a flowsheet using 8 M HF-2 M HNO_3 produces a concentrated dissolver product without requiring separation during dissolution. This dissolvent is highly corrosive to alloys currently used in dissolvers at ICPP, and other materials of construction were examined for this dissolvent. In a two-step dissolution mode, hydrofluoric acid was used as dissolvent to produce a concentrated dissolver product; there has been considerable experience with this reagent in the dissolution of zirconium fuels at ICPP. Due to low solubility of UF_4 in hydrofluoric acid, the bulk of the uranium as U_3O_8 , is removed by a nitric acid leach before the hydrofluoric acid dissolution of the HNO_3 -insoluble uranium; flowsheets, which include separation of the nitric acid leachate from the remainder of the solids, were examined using several concentrations of hydrofluoric acid. Settling velocities were measured for these leached solids to assist in design of equipment for solids separation.

All dissolution studies were made using actual overhead product elutriated from the pilot-plant burner during combustion of unirradiated Rover fuel. Stability and corrosion studies were made using stock solutions of niobium oxide dissolved in hydrofluoric acid together with appropriate reagent grade chemicals.

II. RESULTS AND DISCUSSION

1. DISSOLUTION OF OVERHEAD PRODUCT FROM THE GRAPHITE BURNER

1.1 Nitric Acid Leach of U_3O_8 from Overhead Product

The combustion process for Rover fuels results in an overhead product typically 30 to 70 wt% U_3O_8 , depending upon the fuel being charged and the burner efficiency. Batch laboratory experiments were previously reported^[5] on nitric acid leaching of uranium oxide from the product. These data showed that 99.8 wt% of the U_3O_8 was nitric acid leachable over a range of 6 M to 13 M nitric acid using 5 to 100 times the stoichiometric requirement of nitric acid, volume-to-solid ratios of 2.5 to 25 ml/g, and 7 to 60 minutes contact time. Only 98.3 wt% of the uranium was recovered in 4 M nitric acid using 3 times stoichiometric nitric acid and 7 minutes contact time.

1.2 Description of Non-leachable Components of Overhead Product

Recent burning of Rover fuel in the pilot plant resulted in overhead product containing HNO_3 -insoluble uranium. The uranium compound remaining in the overhead product after nitric acid leaching was identified by x-ray diffraction as Nb_3UO_{10} ^[6]. This compound was prepared in the laboratory by mixing stoichiometric amounts of Nb_2O_5 and U_3O_8 , and heating in an electric furnace at 1550 to 1600°C using a nitrogen atmosphere. At 1000°C, only minor amounts of Nb_3UO_{10} were formed. It was concluded that localized high temperature in the burner contributes to the formation of this non-leachable uranium. Scoping studies showed that either HF or HF- HNO_3 will dissolve this compound, but that nitric acid alone is ineffective. Absorption spectroscopy showed that the uranium was in solution largely in the six valence state, presumably as UO_2F_2 , even with no oxidant present.

Niobium oxide, Nb_2O_5 , is a major component of the overhead product from combustion of Rover fuel. Either HF or HF- HNO_3 mixtures will dissolve niobium oxide, and the rate increases with increasing hydrofluoric

acid concentration up to about 20 M HF. The monoclinic high-temperature form of Nb_2O_5 , which is the major component in the overhead product, and the pseudo-hexagonal form dissolve more rapidly, while the monoclinic zeta form is more resistant to dissolution. The hydrofluoric acid added to dissolve the HNO_3 -insoluble uranium also dissolves a portion of the niobium oxide; the amount of the niobium oxide dissolved affects the waste handling system selected for the process. Total dissolution of the niobium produces a fluoride solution similar to the zirconium waste raffinate which is calcined to a solid form in the Waste Calcination Facility at ICPP.

The overhead product contains an estimated 3 to 7 wt% of the inert solids (unburned carbon and alumina bed material) which will not dissolve in any of the proposed reagents; these are not of interest for the recovery of uranium, but they will require separation from the dissolver product prior to the extraction cycle. Undissolved niobium oxide increases the total quantity of these solids which require separate handling and storage.

1.3 Settling Rates for HNO_3 -leached Solids from Overhead Product

A process using a nitric acid leach prior to dissolution of $\text{Nb}_3\text{UO}_{10}$ must include adequate separation of the non-leachable solids from the nitric acid leachate to prevent excessive losses of uranium. The settling rate for the leached solids from overhead product from two types of fuel was measured 10 cm below the surface in 8M nitric acid leachate using a modified Andreasen method. Figure 1 shows the settling times versus the percent of total solids settled together with the percent of uranium in the solids. These data show that the HNO_3 -insoluble uranium, $\text{Nb}_3\text{UO}_{10}$, is fairly well distributed in the solids, but a slightly higher proportion is present in the smallest particles. In 30 minutes, the uranium settled to below the limit of detection, or 95 wt%; in 60 minutes, 99 wt% of the total solids settled. These data show that specially designed settling equipment could reduce uranium losses from the process to less than 0.4 wt% when overhead product contained 10 wt% HNO_3 -insoluble uranium.

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Fig. 1. Settling rate of HNO_3 -insoluble solids from Rover overhead product in 8M nitric acid leaching liquor. (Fuel with high uranium content produced with jet grinder operating in the graphite burner.)

The nitric acid leached product from combustion of the high uranium loaded fuel contained about 40 wt% unburned carbon and 15 wt% bed material while the leached product from the combustion of low-uranium fuel contained 25 wt% unburned carbon and 4 wt% bed material. These leached products also contained 3 and 5 wt% uranium respectively as $\text{Nb}_3\text{UO}_{10}$ and the remainder was niobium oxide. Data for the two different products, one produced with and one produced without jet grinders operating in the fluidized-bed burner, show that the jet grinders did not reduce the particle size of the elutriated solids. According to analysis, the niobium oxide settles slightly slower than the alumina bed material, while the carbon appears to remain suspended the longest. Assuming niobium oxide density of 4.6 g/cm^3 for all of the leached solids, 50 wt% of the solids were $>10\mu$ diameter while less than 1 wt% were $<3\mu$ diameter.

1.4 Dissolution of Nitric Acid Insoluble Components of Overhead Product

The overhead product used for the dissolution studies was elutriated after fuel combustion was complete during operation of the jet grinders in the fluidized bed burner^[7]. This product contains an unusually high concentration of HNO_3 -insoluble uranium which was of particular interest in these experiments. The composition is approximately 42 wt% U_3O_8 , 39 wt% Nb_2O_5 , 13 wt% $\text{Nb}_3\text{UO}_{10}$, and 6.5 wt% inert residue, mostly Al_2O_3 with small amounts of carbon. The unburned carbon content is considerably lower than the 20-30 wt% expected in normal overhead product^[4]. Dissolution experiments, made to compare hydrofluoric acid and hydrofluoric-nitric acid mixtures as dissolvents of the HNO_3 -insoluble components, showed no difference in dissolution characteristics between this product and a higher-carbon product elutriated during normal burner operation without jet grinders in operation.

In studies using a nitric-acid leach to dissolve U_3O_8 , the overhead product was contacted for two hours with 8 M nitric acid using 10 ml of liquid per gram of overhead product which is approximately five times the stoichiometric quantity of acid required. Following leaching, the non-leachable solids were washed thoroughly with water before contacting with the hydrofluoric acid dissolvents.

Rates of dissolution for $\text{Nb}_3\text{UO}_{10}$ were determined by adding solids into the boiling reagent and dissolving under reflux for the specified time; at the end of this time, the solution was chilled quickly in an ice bath to stop the dissolution, and solids were filtered and washed. The dissolvent was analyzed for uranium and niobium content; water and chromate washes were sometimes analyzed separately to determine the amount of uranium remaining as UO_2F_2 or UF_4 in the filtered solids. The washed residue was analyzed for niobium and residual uranium.

These dissolution data for HNO_3 -insoluble uranium are based on $\text{Nb}_3\text{UO}_{10}$, so that they are applicable to any overhead product irrespective of the HNO_3 -insoluble uranium content of the particular product. The actual uranium loss to the process is considerably lower than the loss of uranium from $\text{Nb}_3\text{UO}_{10}$ as reported; to obtain the process loss, values given must be multiplied by the fraction of uranium which is HNO_3 -insoluble in the original overhead product. The percent of niobium and uranium dissolved is based on the total found in the dissolvent, washes, and residue; the dissolved uranium includes all uranium converted from $\text{Nb}_3\text{UO}_{10}$. The uranium loss is based upon the content of the washed residue.

1.41 Comparison of Dissolvents

A direct comparison of the rates of dissolution of Nb_2O_5 and $\text{Nb}_3\text{UO}_{10}$ in overhead product was made by using the same liquid-to-solids ratio for various reagents; total dissolution of the niobium from the solids would have produced 1 M niobium in solution. All U_3O_8 was removed by a nitric acid leach prior to the rate determination. The rate of dissolution was determined in four acids considered in the proposed flowsheets. The data in Figure 2 show that the rate of dissolution of Nb_2O_5 increased with increasing hydrofluoric acid concentration. At 8 M hydrofluoric acid, the addition of 2 M nitric acid approximately doubles the initial rate but has little effect after the first ten minutes. Figure 3 shows the rates of dissolution of the HNO_3 -insoluble uranium, $\text{Nb}_3\text{UO}_{10}$, at various dissolvent concentrations. This compound is dissolved faster from the leached overhead product than the niobium oxide, and the effect of different concentrations of

Fig. 2. Dissolution rate of niobium oxide (Nb_2O_5) from overhead product. (After a HNO_3 -leach and using a liquid-to-solids ratio to produce 1 M niobium.)

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Fig. 3. Rate of dissolution of $\text{Nb}_3\text{UO}_{10}$ from overhead product. (After a HNO_3 -leach and using a liquid-to-solids ratio to produce 1M niobium.)

hydrofluoric acid is not as evident. The initial dissolution of the uranium is fairly rapid in 6M HNO_3 -2M HF, but the dissolution becomes extremely slow after the first 30 minutes, possibly because it is necessary to dissolve a higher proportion of the Nb_2O_5 in order to contact the remaining uranium compound.

1.42 Rates for a One-step Dissolution

Dissolution rates were determined for two proposed flowsheet conditions which do not include leaching of the overhead product with nitric acid prior to dissolution of the non-leachable uranium. The dilute flowsheet with 6 M HNO_3 -2 M HF using a 60 to 1 liquid-to-solids ratio results in a concentration of 0.04 M niobium in the dissolver product if complete dissolution occurs. The concentrated flowsheet with 8 M HF-2 M HNO_3 using a 3 to 1 liquid-to-solids ratio results in a concentration of 1.1 M niobium in the dissolver product if complete dissolution occurs. Table 1 shows the wt% of uranium and niobium which remains undissolved after a given dissolution time. In both acid mixtures, the uranium dissolves more rapidly and completely than the niobium. Comparison of these data with that given in Figures 2 and 3 shows that a higher liquid-to-solids ratio is highly effective in improving the dissolution of uranium and niobium in 6 M HNO_3 -2 M HF; uranium loss to the process is estimated at only 0.2 wt% if the HNO_3 -insoluble uranium content, as $\text{Nb}_3\text{UO}_{10}$, is 10 wt% of the total uranium. Large quantities of U_3O_8 , which had not been leached by nitric acid, dissolve first and the amount of HNO_3 -insoluble Nb_2O_5 and $\text{Nb}_3\text{UO}_{10}$ dissolved is considerably less during the first five minutes of dissolution at these flowsheet conditions.

1.43 Rates for a Two-step Dissolution

The direct comparison of reagents showed that 22 M hydrofluoric acid was the best dissolvent for both niobium and uranium; however, this reagent has the disadvantage of requiring a two-step dissolution. The U_3O_8 in the overhead product is quickly coated with insoluble UF_4 when contacted with hydrofluoric acid alone, and dissolution of the bulk of the uranium is extremely slow; therefore, a nitric acid leach prior to the hydrofluoric dissolution is required,

TABLE I

DISSOLUTION OF GROSS OVERHEAD PRODUCT AT FLOWSHEET CONDITIONS

(Product dissolved at the boil using liquid-to-solids ratios which produced flowsheet concentrations with no HNO_3 -leach prior to dissolution.)

Dissolvent	Final Nb Conc., M	Component	Wt% of Component Remaining Undissolved			
			Time from Start of Dissolution			
			5 Min	10 Min	30 Min	60 Min
8 <u>M</u> HF-2 <u>M</u> HNO_3	0.04	$\text{Nb}_3\text{UO}_{10}$	20	8	3	3
		Nb_2O_5	46	47	18	8
2 <u>M</u> HF-6 <u>M</u> HNO_3	1.1	$\text{Nb}_3\text{UO}_{10}$	93	35	6	2
		Nb_2O_5	97	69	50	17

TABLE II

DISSOLUTION OF LEACHED OVERHEAD PRODUCT AT FLOWSHEET CONDITIONS

(Rate for HNO_3 -leached product dissolved at the boil using liquid-to-solids ratios which produce proposed flowsheet concentrations.)

Dissolvent	Final Nb Conc., M	Component	Wt% of Component Remaining Undissolved			
			Time from Start of Dissolution			
			5 Min	10 Min	30 Min	60 Min
8 <u>M</u> HF	1.1	$\text{Nb}_3\text{UO}_{10}$	7	9	5	4
		Nb_2O_5	53	62	38	24
22 <u>M</u> HF	3	$\text{Nb}_3\text{UO}_{10}$	--	1.4	0.8	0.5
		Nb_2O_5	--	7.2	4.4	2.9

and additional equipment is necessary to separate the solids from the leachate after the nitric acid dissolution. In order to avoid high mole ratios of fluoride-to-niobium, which lead to instability when aluminum is added to complex excess fluoride, the niobium concentration is increased with increasing concentration of hydrofluoric acid by decreasing the liquid-to-solids ratio used for dissolution. Data are presented in Table II for dissolution at two levels of hydrofluoric acid at flowsheet conditions using a 7.3 mole ratio of fluoride-to-niobium. The 22 M hydrofluoric acid was considerably better as dissolvent than 8 M hydrofluoric with regard to both the niobium and uranium.

Additional dissolutions were made at 14 M, 18 M, and 28 M hydrofluoric acid using 7.3 mole ratio of fluoride-to-niobium and 60 minutes total dissolution time. In all cases, greater than 96 wt% of the niobium and greater than 99 wt% of the $\text{Nb}_3\text{UO}_{10}$ was dissolved. The dissolution rate increased only slightly with increasing acid concentration in the range 14 M to 28 M HF; however, there was a considerable difference in the amounts of precipitated uranium fluorides at the different acid concentrations.

1.5 Uranium Solubility in Dissolver Product

The uranium concentration in dissolver product containing niobium was 30 g/l $\pm$ 10% in a number of dissolutions using 22 M hydrofluoric acid, resulting in uranium salts precipitating and remaining in the solids. Further studies showed the concentration of uranium in saturated dissolver product was dependent upon hydrofluoric acid concentration as shown in Figure 4. Maximum solubility of uranium in solutions with a 7.3 mole ratio of fluoride-to-niobium occurs at about 18 M fluoride and 2.5 M niobium. In dissolver product from dissolutions with 8 M HF-2 M HNO_3 containing 1.1 M niobium, the dissolved uranium concentration was 28 g/l compared to 18 g/l without the nitric acid, indicating that addition of nitric acid increases uranium solubility. The uranium solubility limit was not exceeded at 5.4 g/l uranium in dissolver product from the 6 M HNO_3 -2 M HF flowsheet.

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Fig. 4. Effect of HF concentration of uranium solubility in dissolver product. (Saturated during dissolution at the boil and cooled to room temperature. Solutions contained a 7.3 fluoride-to-niobium mole ratio.)

Both UF_4 and UO_2F_2 were identified by x-ray diffraction in residues which had not been washed following the dissolution in hydrofluoric acid. The UO_2F_2 dissolves readily in water, while the dissolution of UF_4 requires treatment with a boiling solution of CrO_3 . By analyzing the wash solutions separately, a distribution between the soluble uranium, UF_4 and UO_2F_2 was established for uranium dissolved from $\text{Nb}_3\text{UO}_{10}$ with different concentrations of hydrofluoric acid. The data in Table III show that the proportion of UF_4 to UO_2F_2 decreases at higher hydrofluoric acid concentrations. The percent of uranium in the dissolver product was related to the uranium solubility shown in Figure 4. The presence of 0.01 M nitric acid had essentially no effect, but as shown in Table III, 0.1 M nitric acid practically eliminated precipitation of UF_4 . The optimum hydrofluoric acid concentration for the two-step dissolution process is 14 to 18 M with about 0.1 M nitric acid present so that a maximum quantity of the uranium dissolved from $\text{Nb}_3\text{UO}_{10}$ will be soluble in the dissolver product, and essentially no UF_4 will be present to require a CrO_3 treatment for complete dissolution.

2. STABILITY OF NIOBIUM-ALUMINUM-FLUORIDE SOLUTIONS

Fluoride is complexed with aluminum and other complexing ions to prevent corrosion of the stainless steel equipment used for feed adjustment, extraction, and waste handling at ICPP. Previous work with zirconium-aluminum-fluoride (Zr-Al-F) solutions^[8] showed that there is a limited concentration range in which solutions are stable, that is, will not form precipitates for a reasonable period of time. Nb-Al-F solutions were prepared for stability studies in polyethylene bottles by adding stock solutions of niobium dissolved in hydrofluoric acid to stirred aluminum nitrate solutions and immersing in a constant temperature bath at 35°C. Solutions were shaken and examined for visible solids daily during the first two weeks and weekly thereafter for a total of two months. At the end of the study, the solutions with precipitates were centrifuged to permit an estimate of volume percent of solids, and selected solids were examined by x-ray diffraction for identification.

TABLE III

URANIUM DISTRIBUTION IN DISSOLVER PRODUCT AFTER A NITRIC ACID LEACH

(Leached Overhead Product dissolved for 60 minutes at the boil and cooled to room temperature.
Fluoride-to-niobium ratio maintained at 7.3 by increasing solids-to-liquid ratio.)

Uranium Distribution after Dissolution	Concentration of Hydrofluoric Acid Dissolvent					
	8M	14M	18M	22M	22M ^(a)	28M
Uranium Available per 30 ml. during dissolution	0.7g	1.1g	1.4g	1.7g	1.7g	2.2g
Uranium Dissolved in the Dissolver Product	74%	86%	89%	51%	66%	20%
Uranium Present as Insoluble UO_2F_2	9%	6%	6%	36%	34%	59%
Uranium Present as Insoluble UF_4	17%	8%	6%	13%	0.4%	21%

(a) Nitric acid at 0.1 M was present during dissolution.

2.1 Nb-Al-F System

Stability information for systems of niobium and fluoride at three levels of aluminum, 0.2, 0.4, 0.6 M, is presented in Figures 5, 6, and 7. The shaded areas on the curves indicate the region of uncertainty in which additional studies are required before solution compositions can be used for process design. In most cases, precipitates formed within the first hour, but a few solutions remained clear for five to seven days before a precipitate formed. A considerable range of stable compositions were found at 0.2 M and 0.4 M aluminum, but stability decreased at higher aluminum concentrations.

In the case of 0.6 M aluminum, aluminum fluoride was precipitated at fluoride-to-niobium mole ratios of 7.3 indicating that if a complexed stable region exists, it is within the concentration range already examined; a very small stable region may exist within the shaded area indicated. Some of the solutions at higher fluoride-to-niobium ratios may have been metastable and might have precipitated if greater than two months were allowed; at 0.2 M niobium, precipitate formed in five days, while the solution containing 0.4 M niobium and 4 M fluoride was stable for two months, but precipitated in a three month period.

Fluoride-to-niobium mole ratios of 5.6, 6.0, 6.5, 7.3, 10, 20, and 50 were examined. At higher ratios, the fluoride was not completely complexed, and precipitation resulted from high fluoride-to-aluminum ratios similarly to zirconium-aluminum-fluoride systems. The formation of precipitate in solutions containing low fluoride-to-niobium ratios is compared to the degree of complexing of the fluoride in Table IV. The degree of complexing is estimated for this work using the following formula;

$$\text{"Free Fluoride"} = \text{total fluoride} - (5 \times \text{niobium} + 2.5 \times \text{aluminum})$$

The validity of this average value of complexing was verified in the corrosion experiments reported later. Solutions having the highest degree of complexing, that is a negative value for "Free Fluoride", are the least stable. Higher aluminum concentrations apparently contribute

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Fig. 6. Stability of niobium-aluminum-fluoride system containing 0.4 M aluminum. (Solution held at 35°C for 2 months.)

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Fig. 7. Stability of niobium-aluminum-fluoride system containing 0.6 M aluminum. (Solution held at 35°C for 2 months.)

TABLE IV

EFFECT OF EXCESS COMPLEXING UPON STABILITY

(Solutions held at 35°C for 2 months.
Unstable solutions are in parenthesis.)

Niobium and Fluoride Concentration in Solution		"FREE FLUORIDE" Concentration, M (a)		
Mole Ratio F/Nb	Nb Conc. M	Aluminum Concentration in Solution		
		02. M	0.4 M	0.6 M
5.5	0.2	(-0.4)	(-0.9)	(-1.4)
	0.4	-0.3	(-0.8)	(-1.3)
	0.6	-0.2	-0.7	(-1.2)
	0.8	-0.1	-0.6	(-1.1)
6.0	0.2	(-0.3)	(-0.8)	(-1.3)
	0.4	-0.1	-0.6	(-1.1)
	0.6	+0.1	-0.4	(-0.9)
	0.8	+0.3	-0.2	(-0.7)
6.5	0.2	-0.2	(-0.7)	(-1.2)
	0.4	+0.1	-0.4	(-0.9)
	0.6	+0.4	-0.1	(-0.6)
	0.8	+0.7	+0.2	(-0.3)
7.3	0.2	-0.1	-0.6	(-1.1)
	0.4	+0.4	-0.1	(-0.6)
	0.6	+0.9	+0.4	(-0.1)
	0.8	+1.3	+0.8	(±0.3)
10.0	0.2	+0.5	0	(-0.5)
	0.4	+1.5	+1.0	+0.5
	0.6	+2.5	+2.0	+1.5
	0.8	+3.5	+3.0	+2.5

(a) The estimation of "Free Fluoride" is based on the following formula:
 "Free Fluoride" = (fluoride, M) - (5 x niobium, M + 2.5 x Aluminum, M)

to instability because solutions with low "Free Fluoride" and low aluminum did not precipitate. Data indicate that solutions generally are more stable when niobium is the major complexer rather than aluminum.

Three types of solids were identified from the three general areas of instability indicated on the curves. $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ was precipitated from solutions with the high fluoride-to-niobium mole ratios similarly to the Zr-Al-F system. Chemical composition of the other two unidentified species has not been determined. At low fluoride-to-niobium mole ratios, the niobium salt precipitated had a distinct x-ray diffraction pattern; the d-spacings of the major lines are 3.3 Å, 3.9 Å, and 6.55 Å. At low niobium concentrations, where the aluminum-to-fluoride ratio is particularly high due to low total fluoride content, the precipitate is mostly amorphous as might be expected from hydrated hydroxy species. This later precipitate is quite voluminous, according to the volume measurements, even though the total cations precipitated are considerably less than from other unstable solutions.

The volume percent of the precipitates in the unstable solutions were estimated after centrifugation. Over 50 percent of the precipitates were less than 3 vol %, 90 percent were less than 10 vol %, and all were less than 20 vol % of the combined volume of solids and solution.

2.2 Addition of Acid to the Nb-Al-F System

Nitric acid is necessary for extraction of uranium into tributyl phosphate. An addition of 2 M HNO_3 was made to twelve Nb-Al-F solutions which were selected to include a range of "Free Fluoride" concentrations. Table V compares the stability of these solutions to the stability of solutions having the same composition except with no nitric acid added. During the initial ten days, stabilities of solutions were the same with and without nitric acid added. After 10-days, precipitates formed in three of the six stable solutions containing nitric acid. Precipitation probably occurs because the increase in hydrogen ion increases the HF species which is a strong fluoride complexer.

TABLE V

EFFECT OF ADDITION OF HNO_3 ON STABILITY OF Nb-Al-F SYSTEM

Estimated (a) "Free Fluoride"	Concentration, $\underline{\text{M}}$ Nb-Al-F	Days Stable	
		2 $\underline{\text{M}}$ HNO_3 Added	No HNO_3
-1.3	0.2-0.6-1.2	0	0
-1.1	0.4-0.6-2.4	0	0
-1.1	0.2-0.6-1.5	0	0
-0.9	0.6-0.6-3.6	0	0
-0.6	0.4-0.6-2.9	0	0
-0.3	0.2-0.2-1.2	0	0
-0.1	0.4-0.2-2.4	>60	>60
-0.1	0.6-0.6-4.4	0	0
-0.1	0.2-0.2-1.5	>60	>60
+0.1	0.6-0.2-3.6	11	>60
+0.4	0.4-0.2-2.9	35	>60
+0.9	0.6-0.2-4.4	43	>60

(a) See footnote Table IV.

2.3 Addition of Fluoride Complexers to Nb-Al-F System

2.31 Addition of Boron

In the zirconium process at ICPP, boron is added as boric acid to the dissolvent for criticality control of the enriched uranium. The Nb-Al-F system was investigated with respect to addition of boric acid, and data are presented in Table VI. The limited data indicate that addition of boron decreases stability in solutions which are already complexed. A mole of boron complexes an average of four moles of fluoride in the Zr-Al-F system, and apparently, the same value should be used to estimate the quantity of fluoride required to produce a stable solution in the Nb-Al-F system.

TABLE VI

EFFECT OF ADDITION OF BORON ON STABILITY OF Nb-Al-F SYSTEM

Estimated ^(a) "Free Fluoride"	Concentration, <u>M</u> Nb-Al-F	Days Stable	
		0.2 <u>M</u> B Added	No Boron
-0.8	0.2-0.4-1.2	0	0
-0.7	0.8-0.6-4.8	0	0
-0.7	0.2-0.4-1.3	0	0
-0.6	0.4-0.4-2.4	0	>60
-0.4	0.4-0.4-2.6	0	>60
-0.3	0.2-0.2-1.2	0	0
-0.1	0.6-0.6-4.4	0	0
+0.3	0.8-0.6-5.8	4	0

(a) See footnote Table IV. Boron not included in calculations.

2.32 Addition of Uranium

Direct second-cycle extraction of the dissolver product is the basis for the concentrated flowsheet; a uranium concentration of greater than 0.25 M (60 g/l) is required to obtain adequate process throughput. The effect of 0.25 M uranium was determined in both over-complexed and undercomplexed Nb-Al-F solutions which were stable without uranium present. The effect of uranium on stability or corrosion has been insignificant in other fluoride processes at ICPP because the uranium concentration was much lower (0.01 M to 0.02 M). As shown in Table VII, the addition of the uranium made the solutions less stable; however, solutions having uncomplexed "Free Fluoride" prior to adding uranium may be metastable for several days. Based on the available extraction data, selection of a suitable concentrated extraction feed is not feasible; extraction from a complexed solution makes Nb-Al-F solutions more stable, but the fluoride is no longer adequately complexed to prevent excessive corrosion in stainless steel equipment.

TABLE VII

EFFECT OF ADDITION OF URANIUM ON
STABILITY OF Nb-Al-F SYSTEM

Estimated ^(a) "Free Fluoride"	Concentration, <u>M</u> Nb-Al-F	Days Stable	
		0.2 <u>M</u> U Added	No Uranium
-0.4	0.6-0.4-3.6	<1 hr	>60
-0.4	0.4-0.4-2.6	1-2 hr	>60
-0.1	0.4-0.2-2.4	1-2 hr	>60
0	0.2-0.4-2.0	1-2	>60
+0.4	0.6-0.4-4.4	5-7	>60
+0.5	0.4-0.6-4.0	3-4	>60
+0.9	0.6-0.2-4.4	>60	>60
+1.0	0.4-0.4-4.0	5-7	>60

(a) See footnote Table IV. Uranium not included in calculations.

3. CORROSION BY FLUORIDE SOLUTIONS CONTAINING NIOBIUM

Corrosion rates were measured by submerging welded coupons in the solutions at constant temperature for the designated period. Coupons were removed, rinsed and weighed, and overall corrosion rates were calculated in mils per month (mpm).

3.1 Corrosion of Type 347 Stainless Steel in Nb-Al-F Solutions

A scoping study was made to determine if Nb-Al-F solutions could be adequately complexed to prevent corrosion in the stainless steel extraction equipment at ICPP. Data were obtained for welded type 347 stainless steel coupons at 35° and 75°C in a 7-day test using stable solutions which represented a wide range of "Free Fluoride" concentrations. Data reported in Table VIII show that niobium is an effective complexer of fluoride and verify the "Free Fluoride" values estimated using mole ratios of 5 fluoride-to-niobium and 2.5 fluoride-to-aluminum. Undercomplexed solutions produce considerably higher corrosion rates, and the increase in corrosion rate with increasing temperature is even more pronounced. When the fluoride is complexed, additional quantities of complexing ions had little effect at either temperature. Most solutions produced higher rates during the initial 24 hours, but the rates leveled off at 0.2 to 0.4 mpm at 35°C in complexed solutions after the second day. These rates will be adequate for process equipment, although they are somewhat higher than those measured previously for Zr-Al-F systems^[9]. After seven days, end grain attack and very slight knife etching of the weld were observed on some of the coupons having 1 mpm overall rate. There is apparently a very narrow composition range of Nb-Al-F solutions which exhibit both adequate complexing of the fluoride to prevent corrosion and good stability characteristics. The addition of 2 M nitric acid increases the corrosion rates as shown in Table IX. The effect is greater in the solutions with higher total fluoride and a lower "Free Fluoride".

Corrosion rates were also measured in solutions containing 0.25 M uranium. Only solutions with distinctly positive "Free Fluoride" values

TABLE VIII

CORROSION RATES FOR STAINLESS STEEL IN Nb-Al-F SOLUTIONS

Mils/month (mpm) for Type 347 S.S. after 7-day exposure

	"Free Fluoride" Concentration, M ^(a)						
	With 4.4-4.5 M Total F			With 2.2-2.6 M Total F			With 3.6 M F
	+0.9	+0.4	-0.1	-0.1	-0.3	-0.4	-0.4
RATE at 35°C, mpm	18	6	2.3	1.1	1.4	1.0	0.5
RATE at 75°C, mpm	900 ^(b)	35	24	4	5	5	5

(a) See footnote Table IV.

(b) Based on two hours exposure.

TABLE IX

EFFECT OF HNO_3 ON CORROSION OF STAINLESS STEEL IN Nb-Al-F SOLUTIONS

Mils/month (mpm) for Type 347 S.S. after 7-day exposure

	-0.1 M "Free Fluoride" ^(a) With 4.4 M Total F		-0.3 M "Free Fluoride" ^(a) With 2.2 M Total F	
	No HNO_3	2 M HNO_3 Added	No HNO_3	2 M HNO_3 Added
RATE at 35°C, mpm	2.3	4	1.4	1.1
RATE at 75°C, mpm	2.4	39	5	16

(a) See footnote Table IV.

were examined because instability results when uranium is added to solutions which are already complexed. The uranium reduced corrosion rates, and a comparison to previous data showed that approximately 2 moles of fluoride were complexed per mole of uranium. Based on this information, a uranium solution, which is not corrosive upon entering extraction equipment, can create corrosion problems after the removal of uranium by extraction unless additional complexing is achieved during the extraction process. On the other hand, addition of another complexer prior to removal of the uranium will most certainly cause instability in the solution.

A specific ion electrode was used to measure a true free fluoride ion activity in some of the corrosion test solutions. Concentrations of 10^{-3} to 10^{-4} molar were estimated. No correlation was found between the measured free fluoride and the corrosion characteristics of the solutions. The corrosion data for Nb-Al-F solutions with nitric acid added indicate that HF may be the species responsible for the corrosion of stainless steel. A more complete study of the fluoride complexes formed and their stability constants is currently being made at this laboratory.

3.2 Corrosion Rates of Selected Alloys in HNO_3 -HF Solutions

The one-step dissolution process requires a mixture of nitric and hydrofluoric acid for dissolution of all of the uranium. The two-step process using mostly hydrofluoric acid needs 0.1 M nitric acid to eliminate UF_4 solids in the dissolver. None of the alloys currently used at ICPP can withstand these acid mixtures. Work in this laboratory has shown that Incoloy-825 and Inconel-625 are promising for this type of service, especially if the fluoride is partially complexed by the dissolving element. In either continuous or semi-continuous dissolution technique, this is feasible; therefore, all solutions examined contained dissolved niobium to partially complex the fluoride. Four-day scoping tests were made using welded coupons submerged in boiling solutions.

A rate of 0.5 mpm was obtained for Incoloy-825 in a dissolver product from the one-step process containing 8 M fluoride, 1.1 M niobium,

and 2 M nitric acid. Dissolver product from a two-step process containing 14 M fluoride, 1.9 M niobium, and 0.1 M nitric acid produced a rate of 0.4 mpm for Incoloy-825 and 1.0 mpm for Inconel-625. A high fluoride solution, containing 22 M fluoride, 3.0 M niobium, and 0.1 M nitric acid produced a rate of 5.5 mpm in Inconel-625. These scoping studies indicate that Incoloy-825 is better for service in these solutions and that as low a concentration of hydrofluoric acid as possible should be used in the two-step process. The Incoloy-825 coupons showed no visible attack, while the Inconel-625 coupons showed a slight general etching attack after a four-day period.

III. CONCLUSIONS

A nitric acid leach will dissolve only the uranium present as the oxide in the overhead product from a fluidized-bed burning of Rover fuel. When processing some types of Rover fuel, $\text{Nb}_3\text{UO}_{10}$ may be produced, and hydrofluoric acid will be required for complete dissolution of the uranium. Dissolution rates for $\text{Nb}_3\text{UO}_{10}$ from overhead product are acceptable with 6 M HNO_3 -2 M HF and with 8 M HF -2 M HNO_3 using 60 minutes dissolution time and flowsheet ratios of liquid-to-solid. The most complete dissolution of Nb_2O_5 and $\text{Nb}_3\text{UO}_{10}$ from overhead product is obtained using a HNO_3 -leach and 14 M to 28 M HF as dissolvent. Maximum uranium solubility, about 44 g/l, is obtained in a dissolver product containing 18 M HF and 2.5 M niobium. Addition of 0.1 M HNO_3 to the dissolvent prevents precipitation of UF_4 , and excess uranium is precipitated as UO_2F_2 which is readily water soluble. Niobium oxide almost completely dissolves at higher concentrations of hydrofluoric acid, but at lower concentrations undissolved Nb_2O_5 remains with the inert solids, unburned carbon and alpha-alumina bed material. Dissolvers for use with HF - HNO_3 mixtures can be constructed from Incoloy-825 or Inconel-625, based on scoping studies.

In dissolver product solutions, fluoride is partially complexed by niobium. Within a limited range of stable solution compositions, the fluoride can be adequately complexed with additional aluminum to prevent corrosion in type 347 S.S. extraction equipment. In order to assure a workable range of stable compositions in Nb-Al-F solutions, the aluminum concentration should not exceed 0.4 M. Addition of 2 M HNO_3 , 0.2 M boron, or 0.25 M uranium results in the complexing of some of the fluoride, and precipitates are formed in most solutions which are otherwise stable and non-corrosive. Complexed fluoride solutions with greater than 0.25 M uranium, which were proposed for concentrated flowsheets, are not acceptable for extraction feed using current technology and procedures, because solutions which are stable and totally complexed when entering the extraction column will be excessively

corrosive after the uranium is extracted. Addition of another complexer to counteract the effect of extracting the uranium can cause formation of precipitates within the extraction columns if the complexer mixes with the feed before the uranium is completely extracted into the organic phase. These problems can be overcome by using the dilute uranium extraction feed and first-cycle extraction equipment currently used for zirconium fuels at ICPP.

Dilute extraction feeds with low fluoride-to-niobium mole ratios are readily attainable in a two-step process using a HNO_3 -leach followed by dissolution of HNO_3 -insoluble uranium and most of the niobium in 14 M to 18 M HF. Settling rates of leached solids indicate that separation from HNO_3 -leaching liquor is easily obtainable; residual nitric acid assures precipitation of the water soluble UO_2F_2 when the HNO_3 -insoluble uranium concentration in the overhead product is sufficient to exceed the solubility limit of uranium in the dissolver product. A dilute flowsheet using 6 M HNO_3 -2 M HF gives satisfactory dissolution rates, but a high fluoride-to-niobium mole ratio in the dissolver product results in an unstable feed when complexed with aluminum.

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