X-816

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CHEMISTRY—SEPARATION PROCESSES FOR
PLUTONIUM AND URANIUM

OAK RIDGE NATIONAL LABORATORY

Operated By
UNION CARBIDE NUCLEAR COMPANY

UCC

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

ORNL
CENTRAL FILES NUMBER

CF- 56-5-48

DATE: May 14, 1956

SUBJECT: POWER REACTOR FUEL PROCESSING PRELIMINARY REPORT

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ABSTRACT

Fused Salt--Fluoride Volatility Process. An overall decontamination factor of more than 10^5 and a uranium loss of less than 0.1% have been obtained with the fluoride volatility process in laboratory tests.

General Dissolution Studies. Fuels containing stainless steel were carburized or dissolved in molten aluminum and then dissolved in nitric acid. Such fuels were dissolved directly in aqua regia, chromic-nitric acid, or, by anodic electrolysis, in nitric acid.

Uranium was recovered from zirconium fuels by leaching with nitric acid after oxidation, zinc or aluminum alloying, fused salt dissolution, or electrolytic dissolution. Molybdenum-uranium alloy was directly soluble in nitric acid at acceptable rates. The rates of dissolution of uranium alloys with Zr, Nb, Si, and Mo in nitric acid or dilute aqua regia are listed.

Solvent Extraction Studies. Adaptations of solvent extraction processes now in use appear feasible for processing solutions of fuel elements containing difficultly soluble metals.

Zircex Process. Hydrochlorination of a zirconium-containing fuel element produced $ZrCl_4$, which volatilized. Uranium chloride in the residue readily dissolved in nitric acid.

Hermex Process. Massive uranium dissolved rapidly in boiling mercury and was recovered from the cooled amalgam as uranium mercuride by filtering and pressing. Fission product decontamination factors were 10^2 - 10^3 for 3-year-decayed uranium and 15-28 for 45-day-decayed uranium. The uranium mercuride was converted to uranium metal by volatilizing the mercury and melting the uranium in a single step at 1200°C .

INTRODUCTION

Three methods of processing heterogeneous fuel elements from power reactors are being investigated: fluoride volatility, solvent extraction, and Hermex. The fluoride volatility method consists of dissolving the fuel elements in a molten fluoride salt and recovery of uranium by volatilization of UF_6 . The second method consists of preparing a suitable acid solution of the fuel elements or of their contained uranium and recovery of uranium by solvent extraction. The Hermex process consists of dissolving the fuel in boiling mercury and recovery of the uranium or uranium alloy in metallic form by decomposition of the amalgam. The volatility process has been demonstrated on a laboratory scale and large scale tests are under way. Solvent extraction is a well-demonstrated process; however, the preparation of the solvent extraction feed from many fuel elements has been tested only in the laboratory with large scale tests planned for the near future. The Hermex process has been tested only in laboratory scouting experiments.

The first step in any method may be a mechanical one, in which all extraneous parts, such as hinges, end boxes, thermocouples, and side plates are separated from the fertile or fissionable material to minimize process throughput volumes. Cladding materials may be removed from fuel rods by pushing the rod through a die. Since it is not practical to dejacket thin elements such as pins or ribbons, they may be sheared into small pieces to make the uranium accessible.

PART I

1.0 FUSED SALT—FLUORIDE VOLATILITY PROCESS

In the fused salt—fluoride volatility process (Fig. 1) for recovering uranium from heterogeneous reactor fuels, fuel is dissolved in a fused fluoride bath by hydrofluorination, uranium hexafluoride is volatilized out of the fused fluoride by fluorination, and an NaF absorption step is used to remove any volatile activity in the uranium hexafluoride product. This appears to be an attractive nonaqueous method of processing reactor fuels which cannot be easily put into aqueous solution.

1.1 Chemical Development Studies

In preliminary studies of the fluorination step, fluorination of $\text{UF}_4\text{-NaF-ZrF}_4$ at 650°C was shown to require a tenfold stoichiometric amount of fluorine in order to obtain better than 99.9% uranium recovery. The solubility of the product UF_6 in NaF-ZrF_4 results in an induction period in the initial part of the fluorination period, during which time the UF_6 builds up to a saturation concentration before being evolved as a gas. Excess fluorine was required at the end of the process, to act as a carrier gas in reducing the uranium content in the waste salt to an acceptable level. Further work on the fluorination process has demonstrated that only a fourfold stoichiometric amount of fluorine is needed if a 1/1 mixture of fluorine and nitrogen is used for about 75% of the total fluorine requirement, the remaining 25% being used without nitrogen.

Fluorination of $\text{UF}_4\text{-NaF-ZrF}_4$ at 600°C , prepared from UF_4 and pre-fluorinated NaF-ZrF_4 , showed that 95 to 99% of the UF_6 can be volatilized with a F_2/U mole ratio of less than 2/1 in the absence of impurities in the salt. The length of induction period, i.e., the lag in time between the beginning of fluorination and the beginning of UF_6 evolution, was decreased nearly 50% when oxide impurities were eliminated. Study of different methods of dispersing the fluorine in the fused salt failed to show any significant effect on the kinetics of the fluorination process. A simple dip tube in the salt was as efficient as a series of sieve plates for dispersing the gas. The observed small variations in fluorine efficiency with different sieve plate arrangements could not be correlated with this variable and were believed due rather to the use of material which was not perfectly free of oxides.

Fig. 1 Schematic Flowsheet of Fused Salt--Fluoride Volatility Process for Recovering Uranium from Heterogeneous Reactor Fuel.

In the case of long-decayed irradiated uranium dissolved in NaF-ZrF_4 by the hydrofluorination procedure, fluorination resulted in a decontamination factor of greater than 10^3 for all fission product activities except those of ruthenium and niobium. The gross decontamination factor was only 100 to 200. Exploratory studies established that finely divided NaF could be used in two different ways to effectively separate the ruthenium and niobium activities from the UF_6 product. In the first method the NaF bed was used at 650°C , in which case the UF_6 passed through the absorption column while the ruthenium and niobium remained on the bed. Gross decontamination factors of greater than 10^4 were obtained. In the second method the UF_6 and niobium were absorbed on NaF at 100°C , permitting the ruthenium to pass into a cold trap. The UF_6 was desorbed at 100 to 400°C in the presence of a flow of F_2 without much niobium being desorbed. The small amounts of ruthenium and niobium desorbed from this bed were removed from the UF_6 stream by passage through a second NaF bed at 100 to 400°C . A gross beta decontamination factor of about 10^5 was obtained in several consecutive runs in two beds of NaF with the absorption-desorption cycle process. This method appears to be much more attractive than the first method at 650°C with respect to obtaining better decontamination and less corrosion.

The absorption capacity of Harshaw NaF pellets for UF_6 was 0.9 g of uranium per gram of NaF regardless of whether the material was in pellet form or had been ground to 12-40 mesh. Variation of the temperature at which absorption occurred over the range of 75 to 150°C or variation of the UF_6 pressure did not affect the capacity. The observed capacity is about 50% of that expected if the complex $\text{UF}_6 \cdot 3\text{NaF}$ is formed. The theoretical capacity was obtained with analytical grade NaF powder.

The vapor pressure of UF_6 over the $\text{UF}_6 \cdot 3\text{NaF}$ complex was determined by the transpiration method over the temperature range 80 to 320°C . The vapor pressure, p , in millimeters of mercury, was related to the absolute temperature, T , by the expression

$$\log p = 10.88 - 5.09 \times 10^3/T$$

The heat of sorption, obtained from these data by the Clausius-Clapeyron equation, was $+23.2$ kcal per mole of UF_6 . The vapor pressure data indicate

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that the NaF decontamination absorption-desorption step is easily operable, since the vapor pressure of UF_6 over the complex is about 10^{-3} mm at 100°C and more than 100 mm at about 300°C . Further evaluation of the two-bed NaF decontamination procedure showed that the uranium loss could be held to 0.05% or less, even in the case of repeated cycling, by using F_2 as the desorbing gas. The use of N_2 instead of F_2 in the $100\text{--}400^\circ\text{C}$ desorption step results in the removal of over 95% of the UF_6 , so that some substitution of N_2 for F_2 in the process should be possible.

1.2 Engineering Development Studies

Equipment decontamination by flushing with molten sodium zirconium fluoride was ineffective. Nitric-boric acid inhibited with lead nitrate was a good solvent for fluoride salt residues; it corroded Inconel only slowly but attacked nickel very rapidly. Other nitric acid solutions tested were unsuitable because of either poor dissolving power for fluoride salt or high corrosion rate, or both, were aqueous solutions of aluminum nitrate, hydrochloric acid, oxalic acid, disodium dihydrogen versenate, and tetrasodium versenate.

Sampling of molten salt by bucket samplers, cold rods, and evacuated tubes was tested. An opening of at least $1/4$ in. dia was needed for salt to flow into a bucket sampler. No seal for an evacuated tube was found which would both maintain an effective vacuum until the sample was taken and melt readily when immersed in the fused salt without contaminating the salt or the sample.

Designs were completed for an engineering test stand comprising a dissolver, fluorinator, cold traps, fluorine disposal scrubber, and UF_6 hydrolyzer. This equipment will be used to study equipment characteristics and process kinetics at low activity levels. Provisions are made to add adsorption and distillation equipment later. About 400 g of uranium will be processed in one batch.

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PART II

An expanded development effort (Fig. 2) was initiated to adapt the solvent extraction technique now used for solid fuel elements containing uranium or thorium and aluminum to the processing of all types of heterogeneous reactor fuel elements. In all solvent extraction methods now in use, the fuel element is first dissolved in nitric acid before being extracted. In the current program, emphasis is being placed on converting the fuel components (listed below) that are not readily soluble in nitric acid to a nitric acid--soluble form and on modifying the Purex, Thorex, and 25 processes.

<u>Cladding</u>	<u>Cores</u>	<u>Bonding</u>
Aluminum	Uranium	Sodium
Zirconium	Uranium-aluminum	Sodium-potassium
Zircaloy-2	Uranium-chromium	Magnesium
Stainless Steel	Uranium-molybdenum	Zinc
	Uranium-thorium	Aluminum-silicon
	Uranium-zirconium	Bismuth
	Uranium-zirconium-niobium	Nickel
	Uranium dioxide--stainless steel	
	Uranium dioxide	
	Thorium	

Indirect dissolution methods being studied include degradation of the metal by carburization or oxidation, metal alloying, or fused salt dissolution followed by dissolution in nitric acid (see Fig. 3). Direct methods include electrolytic dissolution and dissolution in a strong oxidizing reagent and removal of undesirable ions before solvent extraction.

Nitric Acid-Soluble Materials
(U, Th, Al, UO_2 , Mo)

Stainless Steel

Zirconium

Stainless Steel
or Zirconium

Stainless Steel

Carburization

Oxidation

Hydrochlorination

Metal Alloying

Fused Salt

Nitric Acid
Dissolution

Electrolytic
Dissolution

Aqua Regia or
Nitric-Chromic Acid

Sulfuric Acid

Solvent
Extraction
Feed
Preparation

Fig. 2 Possible Methods for Dissolution of Heterogeneous Reactor Fuel Element Components.

Fig. 3 Schematic Flowsheet for Processing Heterogeneous Reactor Fuel Elements

For the three major classes of fuels, the processes favored at present are:

Metallurgically bonded zirconium fuels: Zircex process, i.e., quantitative removal of jacket and alloy zirconium by hydrochlorination at 300°C to form volatile ZrCl_4 , dissolution of the residue in nitric acid, and removal of chloride by distillation.

NaK-bonded fuels: mechanical dejacketing followed by acid dissolution or other processing method for the core.

Stainless steel--containing fuels: rapid dissolution in aqua regia and removal of chlorides by distillation; titanium equipment would be used.

2.0 GENERAL DISSOLUTION STUDIES

2.1 Stainless Steel--containing Fuels

Preliminary cost estimates indicate that direct dissolution of enriched uranium dioxide-sintered stainless steel fuel clad with stainless steel in aqua regia is more economical than carburization followed by dissolution in nitric acid.

Carburization. Stainless steel can be converted to a nitric acid--soluble form by high-temperature carburization in methane gas. In a series of experiments, 2.5 wt % carbon was introduced into stainless steel in 2 hr at 1100°C . Simulated Army Package Power Reactor fuel element samples (stainless-steel-clad uranium dioxide--sintered stainless steel) were carburized and then dissolved in 3.0 M HNO_3 containing 0.3 M urea at a rate corresponding to 8 hr for a full-size fuel element. The urea was used to react with nitrogen oxides and so prevent passivation of the stainless steel. The insoluble carbide residue, about 27% of the stainless steel, was leached with hot 10 M HNO_3 to recover any remaining uranium dioxide. In three experiments, uranium losses in the solids after the leaching were 0.008, 0.34, and 0.25% of the original uranium.

Molten Aluminum Dissolution. In bench-scale test dissolvings, type 316L stainless steel dissolved in molten 2S aluminum at a maximum rate of 16 $\text{mg}/\text{cm}^2/\text{min}$. The rate dropped to a minimum of 0.36 $\text{mg}/\text{cm}^2/\text{min}$ in a 10% stainless steel melt. With further increase in the stainless steel content of the melt, the dissolution rate increased and appeared to be

leveling off at $7 \text{ mg/cm}^2/\text{min}$ in a 43% stainless steel melt, at which point the test was interrupted by equipment failure. This melt dissolved readily in nitric acid containing $0.005 \text{ M Hg(NO}_3)_2$. The only undissolved material appeared to be aluminum oxide formed by exposure of the high-temperature melt to air during the test.

Aqua Regia Dissolution. Stainless steel dissolved readily in a mixture of nitric and hydrochloric acids in tests to show the feasibility of a proposed flowsheet (Fig. 4). Side reactions, such as formation of nitrosyl chloride, were not excessive. It is important in this process that chloride be removed from the solution after dissolution by distillation in order to avoid corrosion during solvent extraction and waste storage. Experiments showed that the chloride concentration could be reduced, by simple distillation, from 3.0 M to $< 20 \text{ ppm}$, an acceptably low concentration for solvent extraction feed. Titanium, which is reported* to have a corrosion rate of 5 mpy in HCl-HNO_3 , may be a suitable dissolver material.

Nitric-Chromic Acid Dissolution. It has been reported† that chromic acid in nitric acid dissolves stainless steel. At elevated temperatures and high nitric acid concentrations, Cr(III) can be oxidized to Cr(VI) . Therefore, direct dissolution of metals containing chromium in nitric-chromic acid may be autocatalytic if the Cr(III) formed in the initial dissolution can be rapidly oxidized to Cr(VI) . In preliminary studies the dissolution rate was proportional to the chromic acid concentration and was affected by the method of refluxing. The Cr(VI) of the chromic acid is reduced to Cr(III) during the dissolution, and if the Cr(III) can be reoxidized sufficiently rapidly to Cr(VI) , a high rate of continued dissolution of the stainless steel can be maintained. Initial tests showed that the rate of oxidation of Cr(III) to Cr(VI) increased with nitric acid concentration. Therefore, further tests were run with 15 M HNO_3 . Type 304L stainless steel dissolved in boiling 15 M HNO_3 — $0.1 \text{ M H}_2\text{CrO}_4$ at a rate of $0.02 \text{ mg/cm}^2/\text{min}$ (Table 1). When the refluxing condensate was returned to the dissolver through a packed column where it was steam-stripped of the more volatile lower oxides of nitrogen, the Cr(III) was rapidly oxidized to Cr(VI) and the dissolution rate of the metal in the dissolvent increased. When a downdraft condenser was used and the condensate with the dissolved lower

* G. E. Hutchinson and P. H. Permar, Corrosion 5(10), 319 (1949).

† J. E. Truman, J. Appl. Chem. (London) 4, 273 (1954).

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Fig. 4

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Table 1 Dissolution Rates of 304L Stainless Steel as a Function of Method of Condensate Return

Dissolvent: 15 M HNO_3 --0.1 M H_2CrO_4

Time (hr)	Dissolution Rate ($\text{mg}/\text{cm}^2/\text{min}$)	
	Condensate Returned with Downdraft Condenser	Condensate Returned through Packed Column
0.5	0.023	0.022
1.0	0.047	0.049
1.5	0.060	0.063
2.5	0.049	0.088
3.5	0.038	0.11
4.5	0.033	0.13
20.5	0.0043	0.27

Table 2 Rate of Anodic Dissolution of Zirconium in 3 M HCl

Current Density (amp/cm^2)	Wt. Loss per amp-hr (g)	Zr Dissolved per amp-hr (g)	% of Wt. Loss Found as Soluble Zr
0.017	1.53	0.95	62.1
0.067	1.25	0.90	72.1
0.14	1.14	0.90	78.5
0.27	0.88	0.81	96.5

oxides of nitrogen was returned to the boiling solution, the dissolution rate of the metal was initially the same as in the first case; when the chromium had been reduced to Cr(III) by the dissolution reaction, the rate decreased.

The chromic-nitric acid dissolution of stainless steel would require a large volume of dissolver solution per unit area of dissolving surface to maintain the dissolving rate high throughout the entire dissolution, and the utilization of the nitric acid would be low. The dissolution rates obtained so far in this system are unsatisfactorily low for process use.

Electrolytic Dissolution. Stainless steel was dissolved by anodic electrolysis in nitric acid without a catalyst. With 10 M HNO_3 as an electrolyte, the current efficiency with direct current was 76.5 to 78.0% between 50 and 90°C. With 60-cycle alternating current, the efficiency was 59 to 65%. The dissolution rate was proportional to the current density. With 5 M HNO_3 , less gas was evolved than with 10 M. In some cases the off-gas contained only a few per cent hydrogen and therefore would not constitute a hazard under properly chosen conditions.

2.2 Zirconium Containing Fuels

In addition to hydrochlorination (Zircex process, Sec. 4) several methods were investigated for dissolving zirconium containing fuels.

Oxidation. In preliminary experiments, samples of high zirconium-uranium alloy containing tin were completely oxidized in air at 1000°C in 10 hr, and up to 85% of the uranium was recovered by leaching the powdered oxide mass with 8 M nitric acid and then with $\text{NaOH-H}_2\text{O}_2$. When uranium-zirconium alloys containing up to 10 wt % zirconium were oxidized with air at 500°C, uranium recovery by nitric acid leaching of the oxide solids was >99.5%. Uranium oxidation rates were 6 to 10 $\text{mg/cm}^2/\text{min}$ at 500°C. When the oxidation temperature was either increased or decreased, oxidation rates decreased and losses increased.

Oxidation of uranium-niobium alloys was unsatisfactory. More than 0.7% of the uranium remained in the residue from the nitric acid leaching of the oxidation products of alloys containing more than 2 wt % niobium.

With low zirconium-uranium alloy more than 99.5% of the uranium was soluble in 8 M HNO_3 after oxidation. The method is particularly interesting for this latter case, since the 98% uranium-2% zirconium intermetallic compound is explosive in nitric acid, and the danger of explosion is eliminated by conversion of the metal to oxide prior to dissolution.

Molten Zinc Dissolution. Samples of high zirconium-uranium fuel elements formed an alloy with molten zinc in 5 to 10 hr at temperatures above 800°C and Zn/Zr weight ratios of 5/1 to 7/1. In tests on a proposed flowsheet for such fuel elements (Fig. 5), the alloying rate increased with increasing temperature and increasing Zn/Zr ratios. The resulting melt dissolved readily in boiling 8 M nitric acid for all Zn/Zr ratios above 6/1. In several of the experiments, small amounts of solid ZrO_2 that remained after the dissolution contained several per cent of the total uranium. When a small amount of magnesium was added, to give a melt with a zinc/zirconium/magnesium weight ratio of 10/2/1, the uranium loss was less than 0.5%.

Molten Tin and Aluminum Dissolution. High zirconium-uranium fuel elements formed alloys with molten tin and aluminum at about the same rate as with zinc, but the melts did not dissolve so completely in acid.

Fused Salt Dissolution. Zirconium metal dissolves in fused potassium sulfate and in ammonium sulfate. The resultant fused mass was dissolved in water; nitric acid can be added before solvent extraction.

Electrolytic Dissolution. Electrodes of zirconium metal and Zircaloy-2, with alternating current, disintegrated in 15 M nitric acid to form a black scale, which dropped from the surface.

Recovery of the uranium from anodically dissolved uranium-zirconium fuel element sections was poor in initial attempts. About 22% of the uranium was lost in a nonleachable form in the black solids, which have been identified by x-ray analysis as α zirconium metal. As the current density increased from 0.017 to 0.27 amp/cm^2 , the percentage of the total zirconium transferred to the solution as soluble zirconium increased from 62.1 to 96.5% (Table 2).

Acid Leaching of Cores. Unirradiated fuel elements made up of a core of either natural uranium dioxide (Pressurized Water Reactor blanket elements) or 12 wt % molybdenum-88% natural uranium clad with zirconium were cut into

Fig. 5 . Flowsheet for STR Fuel Element Dissolution in Molten Zinc.

0.5-to 1-in. long sections. The uranium dioxide cores dissolved readily in 10 M nitric acid, and the dissolution rate increased as the nitric acid concentration increased. The alloy cores dissolved at satisfactory rates, 1/8 in./hr in 8 M HNO_3 and 1/64 in./hr in 4 M HNO_3 . The amount of uranium-molybdenum alloy that can be dissolved in a given amount of acid is limited by the solubility of molybdic acid. A 3.5 M HNO_3 solution containing 5 g of uranium per liter (0.02 M) was almost saturated with molybdenum but was suitable for solvent extraction.

Thorium plates clad with zirconium have been suggested as blanket elements. In tests to determine the feasibility of shearing these elements into small pieces and leaching the thorium with fluoride-catalyzed nitric acid, thorium samples dissolved 120 times faster than zirconium (120 vs 0.97 mg/cm²/min) in boiling 13.0 M HNO_3 -0.05 M fluoride. This rate was observed when the F/Zr ratio in solution was 4/1. These results indicate that sufficient fluoride ion is dissociated from the ZrF_x complex to catalytically dissolve the thorium and that the bulk of the zirconium will probably not dissolve. In any event, if the zirconium does dissolve, the amount of fluoride used is decreased to a catalytic amount from the stoichiometric amount normally required for dissolution of zirconium.

Acid Dissolution of Core Alloys. Dissolution rates of all alloys tested were satisfactorily fast in 5 M HNO_3 --2 M HCl (Table 3). In boiling 8 M HNO_3 the rates of 2 and 5% niobium alloy were satisfactorily fast but the rate for 15% niobium alloy was too slow, 0.07 mg/cm²/min, for process use (Table 4). When leached with aqua regia, the insoluble residues from molybdenum alloys retained almost no uranium; the niobium alloy residues retained 0.1 to 1% of the uranium; and the zirconium alloys retained 1 to 15% of the uranium (Table 3). Losses appeared to increase slightly with the niobium content and markedly with the zirconium content, but in general were nonreproducible.

Dissolution of molybdenum-uranium alloy in nitric acid is complicated by the insolubility and precipitation of molybdic acid. A solution obtained by dissolving 12% molybdenum--88% uranium alloy was saturated with molybdenum when it contained only 5 g of uranium per liter, which is too low a uranium concentration for efficient solvent extraction processing. Solvent extraction feed that contained about 200 g of uranium per liter was

Table 3 Uranium Losses in Insoluble Residues after Dissolution of Various Alloys

Dissolvent: boiling 2 M HCl--5 M HNO₃

Alloy Composition (%)					Dissolution Rate (mg/cm ² /min)	U Loss to Insoluble Residue (%)
U	Nb	Zr	Mo	Si		
98	2	-	-	-	10.95	0.16
95	5	-	-	-	9.06	0.98
90.3	9.7	-	-	-	13.58	0.05
85	15	-	-	-	6.51	0.57
95	0.5	4.5	-	-	12.33	1.40
93.4	1.33	5.27	-	-	14.68	1.07
99.25	0.12	0.41	0.22	-	32.70	0.02
98	-	-	2	-	12.56	No residue
99.5	-	-	-	0.5	7.60	0.002
97.9	-	2.1	-	-	7.61	1.39
92.5	-	7.5	-	-	9.33	5.97
90	-	10.0	-	-	17.88	9.60
85	-	15.0	-	-	9.46	10.08
80	-	20.0	-	-	6.80	15.27

Table 4 Dissolution of Uranium-Niobium Alloy in Boiling 8 M HNO₃

Alloy		Dissolution Rate (mg/cm ² /min)	U Loss to Insoluble Residue (%)
U(%)	Nb(%)		
85	15	0.3	0.3
95	5	4	0.06
98	2	6	0.07

2.3 Slug Dejacketing

An ORNL aluminum-jacketed uranium slug was successfully dejacketed by being rolled horizontally in a standard sheet-metal-forming roller. The roller has three rolls, each 3 ft long and 4 in. in dia. A Medart rod straightener was used to expand the jacket of an ORNL 4-in.-long slug and an 8-in.-long Savannah River slug. However, the operation could not be completed because of jamming between the guide and expanded jacket. It is believed that slugs 2 ft or longer could be dejacketed with the Medart.

3.0 SOLVENT EXTRACTION STUDIES

Tributyl phosphate solvent-extraction processes are in use for recovering fertile and fissionable materials from nitric acid solutions of fuel elements containing uranium or thorium and aluminum. The 25 process is used to recover uranium from enriched uranium fuel, the Purex process for recovering uranium and plutonium from natural uranium fuel, and the Thorex process for recovering thorium and uranium from thorium fuels. The flow-sheets for these processes are being modified for use with nitric acid solutions of the various heterogeneous reactor fuel elements.

3.1 Enriched Uranium Fuels

Batch countercurrent studies of the 25 process flowsheet with synthetic APPR fuel solution indicated that a feed nitric acid concentration of 3 M is near optimum for efficient uranium recovery (Fig. 7). Approximately three extraction stages, with the extractant 6% tributyl phosphate in Amsco, were required to hold the uranium loss at 0.01%. Stripping data were inconclusive owing to the presence of an emulsifying agent, which made phase separation in the first strip stage difficult. Macro amounts of iron, chromium, nickel, or zinc did not affect process operation.

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ORNL-LR-DWG 10460

Fig. 6 . Schematic Flowsheet for Processing Uranium-Molybdenum Fuels.

Fig. 7
Tentative Flowsheet for First-Cycle Solvent Extraction Processing
of Enriched Uranium- Stainless Steel Fuel Elements. Volumes are
Relative.

3.2 Natural or Moderately Enriched Uranium Fuels

The fuels that will be processed by a modified Purex flowsheet include those containing uranium metal, uranium oxide, uranium-molybdenum alloy, and uranium-zirconium alloy with low zirconium contents. With the irradiation of 3000 Mwd/ton proposed for some of the power reactor fuels, three cycles of extraction may be required.

Results of preliminary solvent extraction tests with dissolved 12% molybdenum--88% uranium alloy indicated that this material may be processed without difficulty by a slightly modified Purex flowsheet. Because of the low solubility of molybdenum in 3.0 M nitric acid, the uranium concentration of the feed to the solvent extraction column is limited to about 5 g/liter. Batch countercurrent extraction and stripping runs with 6% TBP showed that approximately four and one-half extraction and six strip stages were needed for adequate uranium recovery. After four scrub stages, the uranium effluent from the extraction-scrub bank contained less than 2 parts of molybdenum per million parts of uranium. The specified tolerance for molybdenum in recovered uranium is less than 10 ppm.

4.0 ZIRCEX PROCESS

In the Zircex process (Fig. 8) zirconium in the fuel element, either as a jacket or an alloy, is converted to $ZrCl_4$ by passing hydrogen chloride at $300^{\circ}C$ over the fuel element. The volatile $ZrCl_4$ is swept out with the by-product hydrogen gas. Uranium in the fuel is converted to uranium chloride, which is not volatile at this temperature and may be dissolved in situ in nitric acid. An alternate procedure is to raise the temperature of the hydrochlorinator to $600^{\circ}C$, after the zirconium has been removed, to volatilize the uranium chloride before it is dissolved in nitric acid. The nitric acid solution in either case is distilled to remove the chloride.

Results of laboratory-scale experiments indicated that this process may be used for removing zirconium cladding from fuel elements or for quantitatively separating zirconium from a uranium alloy. Zircaloy-2 reacted with HCl at $300^{\circ}C$ at a rate of $2.86 \text{ mg/cm}^2/\text{min}$. The tin in the alloy remained in the metallic state in the form of small pellets and zirconium carbide did not react. Under the same conditions, 20% zirconium--80% uranium reacted at a rate of $5.1 \text{ mg/cm}^2/\text{min}$. The volatilized zirconium tetrachloride contained only 0.0008-0.026% of the total uranium (Table 5). The uranium chloride remained as a powdered residue, of which 99.8% dissolved in dilute nitric acid.

The zirconium tetrachloride sublimate should not be difficult to handle. In experiments with a 2-liter conical air-cooled condenser for removing the zirconium tetrafluoride from the hydrochlorinator off-gas, a fine powdery sublimate was formed which flowed freely from the apex of the condenser.

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Fig. 8. Schematic Flowsheet for the Zircex Process for Dissolution of Zirconium-Uranium Fuel Elements.

Table 5 Distribution of Uranium and Zirconium in Hydrochlorination Reaction

	U(% of Total)		Zr(% of total)	
	Run 1	Run 2	Run 1	Run 2
In sublimate	0.026	0.0008	99.4	99.9
In residue				
Soluble in dilute HNO_3	99.9	99.9	0.26	0.03
Soluble in dilute HNO_3 -HF	0.077	0.04	0.005	0.006
Insoluble	0.042	0.007	0.340	--

PART III

5.0 HERMEX PROCESS

The Hermex process (Fig. 9), a method proposed for recycling and purifying scrap uranium, thorium, or other high-melting metals or alloys and for decontaminating irradiated uranium or thorium, is based on the much greater solubility of such metals in hot mercury than in cold. It consists in continuously dissolving the metal in boiling (356°C) mercury and withdrawing the hot solution, leaving in the dissolver a floating slag containing most of the impurities. To date, work has been concentrated on uranium. Further processing consists in cooling the hot solution to 25°C to precipitate uranium mercuride and recovery of the mercuride as a butter-like quasi amalgam by filtration. The uranium quasi amalgam containing about 1-2 wt % uranium is washed with dilute HCl, and then in a single operation the mercury is volatilized and the uranium is melted to dense metal by slow heating to 1200°C .

In laboratory studies, massive uranium dissolved rapidly, at a rate of 5 to 20 $\text{mg}/\text{cm}^2/\text{min}$, in boiling mercury. Uranium was soluble to about 1 wt % at 356°C and to 0.001 wt % at 25°C . In an initial experiment with scrap Fernald unirradiated uranium, the metal dissolved easily without preliminary cleaning or pickling to remove surface oxide scale. The product met light-metal impurity specifications except for boron and

Fig. 9 Hermex Process

silicon (Table 6), which may have been leached from the glass equipment used. Photomicrographs of uranium samples before and after Hermex processing showed significant removal of solid inclusions (Fig.10). When irradiated uranium was processed, significant gross β and γ decontamination factors were obtained (Table 7). Uranium losses to the slag were 2 to 3%, but are not considered significant because of the small-scale apparatus used in the studies.

An alloy of 2% zirconium--98% uranium alloy dissolved at the satisfactory rate of 5 mg/cm²/min in boiling mercury. The final product metal contained 0.44 wt % zirconium. Zirconium metal dissolved at the very slow rate of 0.03 mg/cm²/min at either 356°C at atmospheric pressure or at 650°C in a pressure bomb.

Table 6 Spectrographic Analysis of Fernald Scrap Uranium

Element	Contamination (ppm)	
	Before Hermex Processing	After Hermex Processing
Al	140	5
B	---	6
Ca	318	5
Cu	140	14
Fe	204	7
Mg	6	0.007
Mn	13	0.03
Ni	---	4
Si	4720	150

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Fig. 10 Photomicrographs showing inclusions in uranium samples.
(a) Fernald scrap as received.

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Fig. 10 Photomicrographs showing inclusions in uranium samples.

(b) Uranium prepared by Hermex processing of Fernald Scrap.

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Fig. 10 Photomicrographs showing inclusions in uranium samples.
(c) High-purity Argonne electrolytic grade uranium.

Table 7. Decontamination Factors for Irradiated Uranium Recovered by the Hermex Process

Feed: Sections of ORNL natural uranium slugs irradiated at 7×10^{18} n/cm² and decayed 3.5 years for runs 1, 2, and 3; irradiated at 2×10^{17} n/cm² and decayed 45 days for run 4

Activity	Decontamination Factor			
	Run 1	Run 2	Run 3	Run 4
Gross γ	100	220	715	15
Gross β	500	410	1080	28
Cs β	1500	2800	---	16 ^a
Sr β	440	1100	---	1450
Rare Earth β	920	800	1300	650
Ru β	3 ^a	1 ^a	10 ^a	2
Zr γ	---	25 ^a	---	10
Nb γ	---	12 ^a	---	6
Pu γ	7	7 ^a	---	1 ^a

^aAccuracy poor as a result of the low levels of initial activity.