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AQUEOUS PROCESSING OF THORIUM FUELS,

PART II

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OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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CONTENTS

	Page
Abstract	1
1. Introduction	2
2. Mechanical Processing	3
2.1 Mechanical Decladding of SRE Fuel	3
2.2 Shear-Leach	7
3. Aqueous Dissolution Methods	22
3.1 Ceramic Cores Clad in Stainless Steel, Aluminum, or Zirconium	22
3.2 Graphite-Base Fuel Elements	29
4. Solvent Extraction	35
4.1 Acid Thorex Process	35
4.2 Acid Interim 23 Process	37
4.3 Kilorod Program	37
4.4 Protactinium Recovery Systems	40
5. Choice of Reprocessing Method	43
5.1 Thorium Fuel Processes	43
5.2 Processing Costs	45
6. References	48

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ABSTRACT

The status of aqueous processing methods for thorium fuels is reviewed. A specially designed 250-ton shear was successfully tested for shearing full-size simulated Consolidated Edison type unirradiated assemblies into 0.25-1.5 in. lengths. Pieces about 0.5-in. long are preferred since the core pellets are more severely crushed during the chopping operation, and consequently, the time to dissolve a core is minimized.

The Darex (dilute aqua regia) and Sulfex (4 to 6 M sulfuric acid) processes for dissolution of stainless steel claddings were developed on a small scale with unirradiated fuel. In hot-cell tests on stainless-steel-clad $\text{ThO}_2\text{-UO}_2$ fuel pins irradiated up to 22,000 Mwd/ton of fuel, the core pellets were severely fractured, and losses of uranium and thorium to the Sulfex and Darex solutions were approximately 0.3 and 3-5%, respectively. The latter losses are easily recovered in the extraction system.

Uranium and thorium can be recovered from graphite-base fuels by burning and dissolving the ash in nitric acid or by grinding to approximately 200 mesh followed by nitric acid leaching.

The Acid Thorex extraction process was developed to recover both uranium and thorium using tributyl phosphate (TBP) as the solvent and the Acid Interim 23 process to recover only the uranium using either TBP or di-sec-butyl phenyl phosphonate as the solvent. The "Acid" processes use nitric acid rather than aluminum as the salting agent. A cost estimate shows that in a plant optimized for the Acid Thorex process where both uranium and thorium are recovered, the overall processing cost (\$8,400/metric ton Th) is only

one third that (\$26,000) for a plant optimized for the Acid Interim 23 process, where only the uranium is recovered. In the AEC conceptual plant the cost for Acid Thorex is only slightly lower (\$26,000 vs \$24,900/metric ton of Th).

1. INTRODUCTION

Work is continuing at Oak Ridge National Laboratory to develop aqueous methods for processing thorium fuels. An extensive survey of ORNL work in this field (ORNL-3219, Part I) was presented at the CNEN Symposium on Thorium Fuel Cycle at Rome in 1961.¹ This survey included aqueous decladding methods, core dissolution and solvent extraction studies, corrosion data, and design criteria. The present paper (Part II) presents recent work on (1) mechanical decladding, shearing, and core-leaching procedures, (2) dissolution of graphite- and carbide-type fuels, (3) advanced solvent extraction methods, and, (4) for continuity, a brief review of previous work.

Objectives of the program are to develop more economical processing methods and to derive the data required to evaluate alternative recycle systems, for example, short-cooled processing (where protactinium is a problem) versus long-cooled processing (where protactinium has disappeared) and also recovery and reuse of thorium vs the exclusive use of fresh, unirradiated thorium in the fuel recycle system. Primary effort has been placed on stainless-steel-clad $\text{ThO}_2\text{-UO}_2$ fuels of the Consolidated Edison type (CETR) and graphite-bearing fuels similar to those proposed for the High Temperature Graphite (HTGR) and Pebble Bed Reactors, with a minor effort on aluminum-clad (Borax IV) or zirconium-clad fuels. The shear-leach (also called, "chop-leach") processing development work was carried out on an engineering scale with a 250-ton shear, using tubular stainless steel assemblies filled with UO_2 , $\text{ThO}_2\text{-UO}_2$, or ceramic cores to simulate actual fuel. SRE core 1 spent fuel was used in the mechanical decladding development program. Cladding

dissolution studies with unirradiated $\text{ThO}_2\text{-UO}_2$ fuels were performed on an engineering scale, but the core dissolution and extraction studies were made only on a laboratory scale with small irradiated fuel pins or tracer levels of activity.

2. MECHANICAL PROCESSING

Mechanical decladding^{2,3,4} and shear-leach^{7,12} methods for processing stainless-steel-clad uranium-thorium metal or oxide fuels were successfully developed and tested on a small pilot-plant scale. Mechanical decladding was used to remove the stainless steel cladding from irradiated NaK bonded, 2.7% -enriched uranium metal Sodium Reactor Experiment Fuel (SRE, Core 1). A similar method could be used to declad the SRE Core 2 fuel (7.8% Th-U). An engineering-scale shear-leach complex consisting of a 250-ton shear and a countercurrent leacher was successfully tested with prototype assemblies consisting of stainless-steel-clad porcelain, UO_2 , and $\text{ThO}_2\text{-UO}_2$. Nuclear Fuel Services will probably use a similar system but with a batch leacher in a commercial fuel processing plant.⁵ A conceptual study for installation of a shear-leach complex at the Idaho Chemical Processing Plant was completed.⁶

Advantages of mechanical processing include: (1) Lower waste-disposal costs than for aqueous decladding. In a comparative cost estimate, waste costs were eight times lower for mechanically decladding² SRE Core 1 fuel and 20 times lower for shearing and leaching⁷ Merchant Ship Savannah fuel, compared with dissolution of the stainless steel cladding in sulfuric acid (Sulfex Process). (2) Reduction of explosion hazard⁹ by removing liquid-metal bonds prior to aqueous fuel dissolution. (3) Shattering of UO_2 or $\text{ThO}_2\text{-UO}_2$ fuel cores during shearing increases the amount of core which can be dissolved per unit of time because of greater surface area.

2.1 Mechanical Decladding of SRE Fuel

Twenty-six SRE-Core 1 irradiated fuel clusters were successfully declad at ORNL in a specially designed² equipment complex (Fig. 1) using the steps shown in Fig. 2. The SRE Core 1 fuel consists of clusters, 105.5 in. long, of seven elements or rods

Fig. 1. Mechanical processing equipment for decladding SRE Core I fuel (interior view, Cell A) ORNL segmenting facility.

Fig. 2. Mechanical decladding of SRE fuel.

containing 2.7% enriched uranium slugs in thin-walled (0.010 in.) type 304 stainless steel tubular cladding, 92-5/16-in. long and 0.790 in. outer diameter. The active fuel length is 72 in., consisting of 12 slugs, 0.750 in. in diameter and 6.0 in. long, of unalloyed uranium thermally bonded to the clad by a 0.010-in. NaK eutectic annulus. At the end of the column is a helium-filled space, approximately 18 in. high, which allows for expansion of the NaK bond and serves as a reservoir for fission gases. The fuel was irradiated to an average exposure of 675 Mwd/tonne and decayed about two years. The fuel was subjected to an undesirably high temperature during a reactor incident in which organic pump coolant leaked into the sodium core coolant.^{8,10} Undesirable fuel characteristics (pitted, swollen, elongated and bent fuel slugs, and partially solidified NaK) were attributed to the incident. The unexpected hardness of the stainless steel may have resulted from work hardening. These characteristics complicated the decladding operation.

About 1.8 metric tonnes of fuel consisting of 175 tubular fuel rods were mechanically declad, steam cleaned, recanned, and placed in dry storage at rates of 2 to 9.2 kg U/hr, with negligible loss of uranium and plutonium. Hydraulic expansion of the cladding and expulsion of the slugs, the primary method of decladding, was effective on 16% of the rods. Slugs from 77% were dislodged by a mechanical screw, the secondary processing method, and 7% had to be processed by a third method using an auxiliary roller-cutter unit followed by peeling of the clad from each fuel slug with a remotely operated manipulator. The primary and secondary methods could not adequately cope with the damaged fuel. Decladding by remote manipulation was successfully used with the damaged fuel, but it is much too time consuming to be practical.

Other stainless-steel-clad, liquid-bonded fuels, such as the SRE Core 2 (7.8% Th-U),⁸ can be declad mechanically if the fuel is not damaged and if the cladding remains ductile. Either hydraulic expansion or the mechanical screw methods are applicable. SRE Core 3, containing UC, could be processed similarly if the carbon content of the core remains less than stoichiometric.¹¹ A greater than stoichiometric amount of carbon in the fuel causes embrittlement of the cladding.

2.2 Shear-Leach

The experimental shear-leach complex (Figs. 3 and 4) was designed to process subassemblies of the type used in the Yankee, Nuclear Merchant Ship "Savannah," Commonwealth Edison, Pressurized Water Reactor (blanket), Consolidated Edison (CETR), or Rural Cooperative reactors or any subassembly whose cross section does not exceed 6.36 x 6.36 in. ORNL prototype assemblies, stainless-steel-clad ceramic "dummies," ThO_2 , or UO_2 , were used in development work (Fig. 5). The 250-ton shear, (Fig. 4) conveyor feeder, and inclined rotary leacher were successfully tested with unirradiated prototype fuel. Interlocking of the components by a fail-safe electrical system for proper operation was highly successful.

After a fuel assembly is placed in the feed envelope of the shear, the mechanical events that follow may be initiated automatically or manually. Prototype assemblies filled with UO_2 were sheared and leached at rates of up to 12 kg of UO_2 /hr. The cost of the shear was \$185,000, and the conveyor feeder and leacher were \$40,000 each. Tests in which stainless-steel-clad UO_2 - ThO_2 fuel prototype assemblies were sheared into 1/2 and 1 in. lengths were satisfactory, and combined shear-leach tests on unirradiated stainless-steel-clad ThO_2 and Zircaloy-2-clad UO_2 is scheduled for early 1963. Irradiated fuel will not be processed.

Shear. — The life of the stepped, moving shear blade (Fig. 6) is estimated at 10,000 cuts of a 36-tube ORNL Mark I assembly filled with porcelain dummies, UO_2 , or UO_2 - ThO_2 . A Squarekeen* No. 3 blade was chipped on the main tooth after 5982 cuts on porcelain-filled ORNL Mark I prototype assemblies. One side of a blade would be used to make 5000 cuts, then turned to the other side for an additional 5000 cuts. Damaged blades could be recovered by grinding the first two steps of the blade to remove the worn edges. The useful life of a single blade is probably sufficient to shear one typical reactor core into 1-in. lengths.

Inner and outer "gags" (Fig. 7) were developed to hold an assembly while it is being sheared. Currently, the shortest terminal piece of fuel assembly that can be held and sheared satisfactorily is 1.5 in. long, the width of the inner gag. A 1-in.-wide

*Composition weight percentage: C-0.53, Mn-0.31, Si-0.87, Cr-5.00, Mo-1.28, W-1.23, S-0.01, P-0.02; hardness, RC-54 to 56; cost \$250.00.

Fig. 3. Shear and leach complex.

Fig. 4. ORNL 250 ton shear assembly.

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Fig. 5. Prototype fuel element Mark I.

Fig. 6. Stepped shear blade for ORNL 250 ton shear.

Fig. 7. Gag for ORNL 250 ton shear.

gag will be tried. Except for this terminal-length limitation, discrete sheared lengths of 1/2 to 2 in. are obtainable. Shearing of fuel into 1/4-in. lengths is not desirable because the clad is severely flattened, trapping pieces of core (Fig. 8). The shortest practical length is probably about 1/2 in.

Brazed fuel assemblies having ferrules as spacers between fuel tubes are easily sheared. Unbrazed assemblies having tube sheets (Fig. 5) as spacers can be sheared as easily as brazed fuel. Near the tube sheets, however, undesirable chunks of fuel held together by the sheet itself are produced. These chunks cannot be handled in a continuous countercurrent leacher because they cannot be completely submerged in the counterflowing acid. Also, the chunks may block the flow of solids in a continuous leacher in which dimensions are minimized because of criticality considerations.

A batch leacher may be required for fuels containing tube sheets. The size distribution of particulate composites composed of cladding, core and braze metal which were dislodged during the shearing of (a) porcelain, (b) UO_2 , and (c) $\text{UO}_2\text{-ThO}_2$ -filled, ORNL stainless-steel-jacketed prototype fuel into 1/4, 1/2, 1, and 1-1/2-in. lengths are presented in Fig. 9. Curves of the particle-size distribution of each component are available.¹² Generally, sheared UO_2 -filled and $\text{UO}_2\text{-ThO}_2$ -filled assemblies produce equal quantities of particles. The amount of UO_2 and stainless steel dislodged increases as the length of sheared pieces is decreased (Table 1).

The cladding of two porcelain-filled Mark 1 assemblies was carburized prior to shearing to simulate hardening and embrittlement of fuel cladding from neutron bombardment in a reactor. Carburization had two effects: (1) More core and clad were dislodged, Table 2 and Fig. 10, than from an untreated assembly. (2) The tonnage required was only about half that required for an uncarburized assembly. In tests by Goode, using a small single-tube shear, the amount of particles dislodged when shearing single tubes of stainless steel or Zircaloy-2 filled with UO_2 pellets irradiated to approximately 16,000 Mwd/ton U did not differ significantly from the amount produced from unirradiated specimens¹³ ($\sim 6\% < 10$ mesh for 1 in. of length) although the irradiated fuel pellets were shattered ($0.1\% < 10$ mesh) during the irradiation period prior to shearing. Measurements of the amount of particles contributed individually by the clad and core were not made.

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Fig. 8. Comparison of stainless steel tubing when shearing a porcelain-filled ORNL Mark I prototype fuel assembly into 1/4-, 1/2-, and 1-inch sections using a stepped blade and ORNL 250 ton shear. Dislodged porcelain fines are not shown.

Table 1. Distribution of UO_2 and Stainless Steel Particles from a Sheared ORNL Mark 1 Fuel Assembly

ORNL Mark 1 assembly: square bundle, 3.625×3.625 in., of 36 type 304 stainless steel tubes, $1/2$ in. OD $\times$ 72 in. long $\times$ 35 mil wall, assembled with $1/4$ in.-OD $\times$ 1-in.-long Kanigen or Nicro brazed spacer ferrules at ~ 12 -in. spacing. Tubes filled with UO_2 pellets, 0.420 in. OD $\times$ 0.625 in. long.

Sheared Length (in.)	UO_2 (Wt %) ^a			
	Dislodged			Retained in Clad
	$<44 \mu$	44-1,000 μ	1,000-9,520 μ	
0.5	22.4	57.6	4.5	15.5
1.0	7.35	25.6	2.4	64.6
1.5	4.5	12.0	1.2	82.3
	Stainless Steel (Wt %) ^b			
	Dislodged			Retained
0.5	0.023	0.38	7.6	92.0
1.0	0.007	0.12	2.1	97.8
1.5	0.003	0.057	2.6	97.4

Wt % computations: (a) $\frac{\text{Weight (g) of } \text{UO}_2 \text{ dislodged}}{\text{Weight (g) of } \text{UO}_2 \text{ in fuel assembly}} \times 100$

(b) $\frac{\text{Weight (g) of stainless steel dislodged}}{\text{Weight (g) of stainless steel in fuel assembly}} \times 100$

Fig. 9. Distribution of total particles smaller than 9520 U dislodged from the shearing of porcelain, UO_2 , or $\text{UO}_2\text{-ThO}_2$ -filled ORNL Mark I fuel into 1/4-, 1/2-, 1-, and 1-1/2-in. lengths.

Table 2. Distribution of Particles from UO_2 , Porcelain, and Carburized Porcelain-Filled ORNL Mark 1 Fuel Assemblies Sheared into 1-in. Lengths

ORNL Mark 1 assembly: square bundle (3.625×3.625 in.) of 36 type 304 stainless steel tubes $1/2$ in. OD $\times$ 72 in. long $\times$ 35 mil wall, assembled with $1/4$ in.-OD $\times$ 1-in.-long Kanigen or Nicro brazed spacer ferrules at ~ 12 in. spacing. Tubes filled with 0.420-in.-OD $\times$ 3-in.-long porcelain sections or UO_2 sections, 0.420 in. OD $\times$ 0.625 in.

	Core Material (Wt %) ^a			
	Dislodged			Retained in Clad
Core Material	<44 μ	44-1,000 μ	1,000-9,520 μ	
UO_2 (Ductile clad)	7.4	25.6	2.4	64.6
Porcelain (Ductile clad)	3.0	16.2	4.3	76.5
Porcelain (Carburized 0.8% max, clad)	3.5	24.0	16.0	56.5
	Stainless Steel (Wt %) ^b			
	Dislodged			Retained
UO_2 (Ductile clad)	0.007	0.12	2.1	97.8
Porcelain (Ductile clad)	0.03	0.108	2.5	97.4
Porcelain (Carburized clad)	0.0165	0.115	5.2	94.7

Wt % computations: (a) $\frac{\text{Weight (g) of core material dislodged}}{\text{Weight (g) of core material in fuel assembly}} \times 100$

(b) $\frac{\text{Weight (g) of stainless steel dislodged}}{\text{Weight (g) of stainless steel in fuel assembly}} \times 100$

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Fig. 10. Comparison of single cut made on carburized ($2.6\% C_{\max}$) and ductile stainless-steel-clad, porcelain-filled ORNL Mark I prototype fuel assemblies.

A bellows-sealed flapper valve¹⁴ (Fig. 11) was developed for use in the feed chutes or discharge ports of the chop-leach complex. The valve was designed to pass solids downward in the open position without constriction of the chute. When the valve is closed the flapper disk seals against rising leacher fumes by seating against an inverted fixed seat. The inverted position prevents trapping of solids and fouling of the seal. The useful life of the valve, based on one cycle per hour, was estimated from tests¹⁴ to be about four years.

Leaching. — In the shear-leach complex, sheared fuel is leached counter-currently with boiling nitric acid in an inclined, rotary spiral leacher. The leacher consists of an inner cylinder into which is welded an internal spiral containing vertical-slot-type weirs (Fig. 3). Solids and liquid are elevated countercurrent to boiling acid flowing through the weirs. Leaching takes place in the lower four stages of the spiral, and washing of the leached clad occurs in four upper stages.

To ensure submergence of sheared fuel under the acid dissolvent, the slip angle for 1.5-, 2.25-, and 3.0-liter batches each of empty type 304L stainless steel tubing (1-in. long), solid stainless steel rod (1/2-in. in diameter x 1 in. long), and stainless-steel-jacketed, porcelain-filled Mark 1 elements sheared into 1-in. lengths were measured at leacher elevations of 10, 20, and 30°. There was little difference in the slip angle of equal volumes of empty cladding, solid stainless steel rods, and porcelain-filled Mark 1 elements. The angle of slip increased with batch volume and less significantly with leacher elevation. At a leacher elevation of 15°, the slip angle increased from about 28 to 32° when the batch volume increased from 1.5 to 3 liters. The optimum leacher batch size is 2.25 liters of sheared Mark 1 prototype, which is equivalent to 8 in. of length.

The slip angle is defined as the counterclockwise angle of rotation of the leacher (looking into the feed end of the leacher) sufficient to bring an originally horizontal batch to the point of slippage (Fig. 12). Slippage first occurs when approximately half of the batch is above the liquid level. To ensure submergence of chopped fuel as it is advanced each flight, the leacher is rotated 360° plus the slip angle (~28° for a 2.25-liter batch) then reversed by the amount of the slip angle.

Fig. 11. Exploded view of bellows sealed flapper valve.

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Fig. 12. Cross-section of leacher from feed end showing slip angle.

Leaching of unirradiated UO_2 -filled ORNL Mark 1 prototype fuel sheared into 1/2, 1, and 1-1/2-in. lengths was accomplished successfully, with negligible loss of uranium. A typical curve of uranium loading (g/liter) vs dissolution time (min) is presented in Figure 13 for 7 M HNO_3 fed at a rate of 4 g-moles HNO_3 /g-mole UO_2 . At this acid strength and ratio, apparent steady state was attained at about the fifth hour. For all sheared lengths tried, a growing inventory of UO_2 was recorded (Figure 14). Increasing the acid-to- UO_2 ratio from 4 to 6 eliminated the UO_2 inventory after the third hour. Mixed ThO_2 - UO_2 leach tests will be made in 1963. An increased residence time will be required to dissolve this fuel. Since both irradiated and unirradiated fragmented fuel (8-20 mesh) was >99% dissolved in 5 hr in batch tests^{15, 1} (Sec 3.1.5), a residence time of 10-15 hr should be adequate for the continuous leacher.

3. AQUEOUS DISSOLUTION METHODS

3.1 Ceramic Cores Clad in Stainless Steel, Aluminum, or Zirconium

These fuel claddings can be dissolved in a suitable reagent prior to dissolution of the oxide core in boiling 13 M HNO_3 --0.04 M HF.¹⁵⁻²⁸ Two head-end processes for Thorex solvent extraction, Darex and Sulfex, were developed on a laboratory and small engineering scale for dissolution of CETR fuel. In the Sulfex process^{15-18,20,22,23} the stainless steel cladding is dissolved in boiling 4 to 6 M sulfuric acid, whereas the cladding is dissolved in dilute aqua regia in the Darex process.^{15-17,19,21-23} Hot-cell experiments^{15,22} show that the Sulfex process will probably be satisfactory for highly irradiated elements but that losses of uranium to the decladding solution are excessive with the Darex system. The BORAX-IV core was processed²⁸ at the Idaho Chemical Processing Plant (ICPP) with a process²⁷ that involved dissolution of the aluminum cladding in NaOH - NaNO_3 , dissolution of the lead bond in dilute nitric acid, and dissolution of the ThO_2 - UO_2 core in 13 M HNO_3 --0.04 M NaF.

3.1.1 Dissolution of Stainless Steel Cladding in Sulfuric Acid

In the Sulfex process for CETR fuel^{15-18,20,22,23} (Fig. 15), the 30-mil stainless steel cladding is dissolved in three times the stoichiometric amount of boiling 4 to 6 M

Fig. 13. Uranium loading as a function of dissolution time for a 4 stage rotary leacher.

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Fig. 14. Uranium inventory in rotary leacher versus dissolution time.

Fig. 15. Decladding and dissolution of Consolidated Edison reactor fuel by the Sulfex-Thorex process.

H_2SO_4 in 1 to 3 hr. About 1.1 moles of hydrogen off-gas are evolved when 55 g (1 mole) of stainless steel is dissolved. The stainless steel cladding is often passive due to either a protective oxide film or traces of nitric acid in the solution. Brazed elements, however, are usually not passive. If passivation occurs, it is most conveniently broken by contacting the element with steel wool.

Losses of uranium to the decladding solution from high-density (greater than 95% of theoretical) fuel specimens were generally less than 0.3% and were not greatly affected by burnup over the range of 620 to 20,000 Mwd per ton of core.^{15,22} The increase in loss with burnup is attributed to the larger surface area present as the result of shattering of the highly irradiated fuel specimens. These results indicate that the Sulfex process will be suitable for the decladding of highly irradiated $\text{ThO}_2\text{-UO}_2$ reactor fuels.

3.1.2 Darex Decladding

In the Darex process for CETR fuel^{15-17,19,21-23} (Fig. 16), the stainless steel cladding is dissolved in sufficient boiling 5 M HNO_3 --2 M HCl to yield a solution containing about 50 g of stainless steel per liter. The off-gas contains 20% NO_2 , 35% NOCl , 35% N_2 , and traces of N_2O , NO , HCl , Cl_2 , and H_2 . Dissolution of a 30-mil-thick cladding requires about 2 hr.

The uranium loss to the Darex decladding solutions was excessively high from highly irradiated CETR fuel specimens;^{15,22} the loss increased from 0.15 to 5% as the burnup increased from 0 to 20,000 Mwd per ton of core. Fragmentation of the fuel pellets undoubtedly contributed to the high losses, but the losses were higher than expected from fragmentation alone. If the Darex process is used, the uranium and thorium can be recovered in the Acid Thorex solvent extraction system (see Sec 4.).

3.1.3 Aluminum Dissolution

Aluminum cladding from $\text{ThO}_2\text{-UO}_2$ fuels such as the BORAX-IV is readily dissolved²⁷ in NaOH-NaNO_3 solutions, with a uranium loss of less than 0.2%. The BORAX-IV fuel, which contained a lead bond between the $\text{ThO}_2\text{-UO}_2$ fuel and the

Fig. 16. Decladding and dissolution of Consolidated Edison reactor fuel by the Darex-Thorex process.

aluminum cladding, was processed at ICPP²⁸ by the method developed at ORNL.²⁷ The aluminum cladding was dissolved in caustic, and the lead bond was dissolved in dilute nitric acid prior to dissolution of the core in 13 M HNO₃-0.04 M HF.

3.1.4 Zirconium Dissolution

Preliminary experiments¹ with unirradiated ThO₂-UO_{2.7} fuel specimens (4.2% UO_{2.7}, 83% of theoretical density) indicated that the zirconium cladding could be dissolved in boiling 6 M NH₄F--1 M NH₄NO₃ (Zirflex process²⁴⁻²⁶), with attendant uranium and thorium losses of less than 0.4%. Losses would undoubtedly be even lower with higher-density UO_{2.0} fuel pellets.

3.1.5 ThO₂-UO₂ Core Dissolution

Thorium metal, thorium oxide, and ThO₂-UO₂ mixtures dissolve in boiling nitric acid containing small amounts of hydrofluoric acid as catalyst.^{1,17,29} Dissolution of high-density fuel pellets (greater than 90% of theoretical) in the optimum reagent, 13 M HNO₃--0.04 M HF, is relatively slow, however. In three times the stoichiometric amount of this reagent, 25 to 40 hr are required to dissolve completely typical 0.26-in.-diam CETR fuel pellets.

The rate of dissolution of ThO₂-UO₂ mixtures containing up to 10% UO₂ depends on the nitric acid concentration, the hydrofluoric acid concentration, the thorium concentration in solution, and the density and state of subdivision of the mixture. When other variables are constant, the rate is maximum when the nitric acid and hydrofluoric acid concentrations are 13 and about 0.06 M, respectively. The instantaneous dissolution rate decreases by a factor of about 5 as the thorium concentration in solution increases from 0 to 0.9 M. Rates of dissolution of ThO₂--4.4% UO₂ pellets (density, 95% of theoretical) in solutions containing 0.04 M NaF were correlated by:

$$R = 0.627 \left(\frac{M}{10} \right)^3 - 0.336 \left(\frac{M}{10} \right)^4 - 0.12 \left(\frac{M}{10} \right)^3 M_{Th},$$

where R is reaction rate, mg g⁻¹ min⁻¹; M is nitric acid concentration in the dissolvent, molarity; and M_{Th} is thorium concentration in the dissolvent, molarity. The dissolution

rate of ThO_2 --5% UO_2 pellets decreases with increasing pellet density; the initial rate in boiling 13 M HNO_3 --0.04 M NaF --0.1 M $\text{Al}(\text{NO}_3)_3$ decreased from 18 to about $1 \text{ mg min}^{-1} \text{ cm}^{-2}$ as the pellet density increased from 60 to 95% of theoretical. The rates of dissolution of ThO_2 and ThO_2 - UO_2 pellets containing up to 10% UO_2 were practically the same when the other conditions, such as pellet density, were constant.²³

Fused ThO_2 , as expected, dissolved more slowly than material of lower density. For example, in 5-hr experiments with -4 to +8 mesh samples, only about 30% of the fused ThO_2 sample dissolved in a 200% excess of boiling 13 M HNO_3 --0.04 M NaF --0.1 M $\text{Al}(\text{NO}_3)_3$, compared with 88% of a sample of 95.8% ThO_2 -- UO_2 .³⁶ which was 93% of theoretical density.²³ Both unirradiated and irradiated (15,000-20,000 Mwd/T) 8- to 20-mesh fuel samples were greater than 99% dissolved in a 5-hr reaction with a 200% excess of boiling 13 M HNO_3 --0.01 M NaF --0.1 M $\text{Al}(\text{NO}_3)_3$. The small residue was dissolved in a second digestion with fresh reagent.¹⁵ Soluble neutron poisons, H_3BO_3 or $\text{Cd}(\text{NO}_3)_2$, can be added to the dissolvent in concentrations up to 0.1 and 0.075 M , respectively, without affecting the rate of dissolution.

3.2 Graphite-Base Fuel Elements

Advanced graphite-base reactor fuel elements will probably contain 150 to 400 μ -diam UC_2 - ThC_2 fuel particles coated with 25 to 60 μ of pyrolytic carbon dispersed throughout a graphite matrix. Representative fuels are the HTGR and the PBR. Several aqueous methods for processing graphite-base fuels have been investigated.³⁰⁻³³ For elements containing coated fuel particles, however, only two methods appear applicable. These are: burning in oxygen followed by dissolution of the ThO_2 - U_3O_8 ash in boiling 13 M HNO_3 --0.04 M F , or fine grinding, probably to 200 mesh to ensure rupture of all the fuel particles, followed by acid leaching to recover the uranium and thorium. At present, the combustion-dissolution approach appears more attractive since both fine grinding and separation of the leach liquor from the residual fines by filtration or centrifugation are difficult. An extensive study has been made of the reactions of thorium and uranium carbides and graphite with H_2O , HCl , H_2SO_4 , or HNO_3 .^{34,35}

3.2.1 Combustion-Dissolution

Combustion (in oxygen at temperatures above 700°C) of graphite-base fuels followed by dissolution of the oxide ash leads to quantitative recovery of uranium and thorium from fuels containing carbon-coated fuel particles^{32,33} (Table 3). This method may also be applicable to fuels containing BeO-coated particles, using procedures developed for the dissolution of sintered BeO;³⁶ however, alumina-coated fuels probably cannot be processed by an aqueous method because of the chemical inertness of sintered Al₂O₃. The Al₂O₃-coated particles remain virtually intact after burning and would have to be crushed to allow recovery of the uranium and thorium by an aqueous dissolution process.

Considerably more effort will be required to develop fully the combustion-dissolution method. Particular attention will be given to methods for treating the radioactive off-gas, to design of the burner (preferably one in which both burning and dissolution can be conducted), and to the evaluation of materials of construction suitable for the burner.

Table 3. Uranium and Thorium Recovery from Graphite-Base Fuels by the Combustion-Dissolution Process

Conditions: Fuel burned in oxygen at 700-900°C; ash digested for 6 to 10 hr in boiling reagent

Fuel	Fuel Comp. (%)		Leachant	Recoveries (%)	
	Uranium	Thorium		Uranium	Thorium
Uncoated UC ₂ -ThC ₂	1.7	8.0	13 M HNO ₃ -- 0.04 M HF-- 0.1 M <u>Al</u> (NO ₃) ₃	100	100
Pyrolytic carbon-coated UC ₂ -ThC ₂	9.9	33.0	13 M HNO ₃ -- 0.04 M HF-- 0.1 M <u>Al</u> (NO ₃) ₃	100	100
Al ₂ O ₃ -coated UO ₂	8.0	0.0	10 M <u>Al</u> HNO ₃	9.9	---

3.2.2 Fine Grinding Followed by Acid Leaching

After a fuel that contains carbon-, BeO-, or Al₂O₃-coated fuel particles is ground fine enough (about 200 mesh) to ensure rupture of the particles, the uranium and thorium can be recovered^{32,33} by leaching with either nitric acid or a mixture of nitric and hydrofluoric acids (Table 4). Digestion for 6 to 8 hr with the boiling reagent is required to effect high recoveries. It is probable that hydrofluoric acid will be required in the reagent to ensure adequate recoveries, although there are too few data to allow a final conclusion.

Table 4. Uranium and Thorium Recovery from Graphite-Base Fuels by the Grind-Leach Process

Conditions: Fuel ground to 200 mesh and leached for 6 to 8 hr with boiling reagent

Fuel	Fuel Comp. (%)		Leachant	Recoveries (%)	
	Uranium	Thorium		Uranium	Thorium
Al ₂ O ₃ -coated UO ₂	8.0	0.0	15.8 M HNO ₃	99	--
Pyrolytic carbon-coated UC ₂ -ThC ₂	9.7	33.8	15.8 M HNO ₃	~99	99.9
Pyrolytic carbon-coated UC ₂ -ThC ₂	9.6	33.5	13 M HNO ₃ -- 0.04 M HF-- 0.1 M Al(NO ₃) ₃	99.4	99.9

Two major problems remain to be solved with the grind-leach process. First, the feasibility of grinding coated-particle fuels to the desired fineness on a large engineering scale must be demonstrated. Second, suitable equipment must be designed for separation of the solids from the acidic leach slurries by centrifugation or filtration.

3.2.3 Reactions of Thorium and Uranium Carbides with Water and Nitric Acid

Reactions of thorium and uranium carbides in various aqueous reagents are being studied to provide basic process data.^{34,35} Hydrolysis of uranium and thorium carbides in water at 80°C results in the formation of the respective solid hydrous oxides and mixtures of hydrogen and hydrocarbons. The nature of the hydrocarbon products depends on the carbide being hydrolyzed. The two monocarbides, ThC and UC, yield a gas consisting of 83% methane and 13% hydrogen on hydrolysis. All the carbide

carbon is converted to gaseous products (Table 5). In contrast, hydrolysis of the higher carbides, U_2C_3 , ThC_2 , UC_2 , results in much less gas evolution. However, the gas contains 30-40% C_2 - C_8 hydrocarbons and 50-80% hydrogen. Furthermore, 50-80% of the carbide carbon remains as nonvolatile carbon compounds. Hydrolysis of the respective carbides yields about the same gaseous products in 6 N HCl and 6 M H_2SO_4 as in water. On the other hand, reaction of UC with 4 M HNO_3 gives completely different results. The off-gas is comprised mainly of NO and CO_2 and contains no hydrogen or hydrocarbon gases (Table 6). In addition, 30-50% of the carbide carbon remains in solution as a mixture of oxalic, benzene polycarboxylic, and higher-molecular-weight organic acids. No insoluble wax is formed. The soluble acids should not constitute a process hazard, however, since they are not nitrated. Similar reactions are expected between other uranium and thorium carbides with nitric acid, but quantitative studies have not been completed. Initial tests show that no solid or waxy residues are formed.

The most reactive carbides are UC, ThC, and ThC_2 , and they hydrolyze completely in a few hours at 80°C, whereas about 24 hr are required for U_2C_3 and UC_2 at the same temperature (Fig. 17). Specific reaction rates cannot be obtained because samples (3-4 g each) disintegrate to powder within approximately 30 min. But in any event the rate of reaction of massive pieces is not dangerously fast under any conditions, even at the boiling point. At room temperature, as expected, the rates of reaction are much lower. For example, complete hydrolysis of 3- to 4-g samples of UC and ThC requires about a week at 25°C.³⁴

The data given above indicate that the best method for processing sodium-bonded UC or UC-ThC fuels clad in a metal such as stainless steel is shearing followed by steaming or reaction with liquid water to destroy the bond and hydrolyze the carbide core. With stoichiometric or substoichiometric carbides, all the carbide carbon will be evolved, and the hydrous oxide residue from the steaming operation will dissolve readily in nitric acid, yielding a solution free from organics. However, if the fuel contains higher carbides, waxes will remain from the steaming operation. These waxes react with nitric acid to yield as-yet-unidentified organic products. These organic products could be a mixture of acids similar to that obtained from the UC- HNO_3 reaction; in this case, there should be no problem presented to further processing.

Fig. 17. Relative rates of hydrolysis at 80°C of 3 to 4 g samples of uranium and thorium carbides in water.

Table 5. Hydrolysis of Thorium and Uranium Carbides in Water at 80°C

	Type of Carbide				
	UC	ThC	U ₂ C ₃	UC ₂	ThC ₂
Volume of gas evolved, ml (STP) per gram of carbide	96	92	61	44	65
Composition of off-gas, vol %					
Hydrogen	13	13	58	45	78
Methane	84	82	2.5	15	1.5
Saturated C ₂ -C ₈ hydrocarbons	2.4	3.5	32	31	8.1
Unsaturated hydrocarbons	0.3	1.3	7.7	9.0	12.4
Nonvolatile carbon compounds, % of original carbon	0	2	48	67	77

Table 6. Reaction of UC with 4 M HNO₃

Product	% of Total Carbon in Product	Product Composition
Off-gas	50-70	77% NO; 19% CO ₂ ; 4% N ₂ O; trace CO; no hydrogen or hydro- carbons.
Soluble organic acids	30-50	20-30% mellitic acid; 5-10% oxalic acid; remainder, benzene and poly- nuclear polycarboxylic acids; product is not nitrated.

The reaction of graphite with nitric acid was also studied briefly because of its importance in processes involving the nitric acid leaching of powdered graphite-base fuels. Reaction is very slow: With finely powdered graphite, only 60-80% of the carbon reacted in 500 hr with boiling 16 N HNO₃. Less than 2% reacted in 24 hr, with up to 20% of the reacted carbon remaining in solution as a mixture of benzene and

higher-molecular-weight polycarboxylic acids. As in the case of the UC-HNO₃ reaction, the products were not nitrated and should not constitute a hazard to the process.

4. SOLVENT EXTRACTION

"Acid" solvent extraction processes have been developed for the extraction of uranium-233 (Acid Interim 23 process)³⁷ or co-extraction of uranium and thorium (Acid Thorex process)³⁸ from nitric acid solutions with tributyl phosphate (TBP) or di-sec-butyl phenyl phosphonate (DSBPP). These processes are designed for systems where criticality is a major problem, and they differ from previous flowsheets³⁹ in that nitric acid is used as the salting agent, rather than aluminum. Decontamination and uranium or thorium recovery with the "Acid" processes are equal to those of the older methods. Advantages include a large reduction in evaporated waste volumes because of elimination of aluminum and, in the case of the Acid Thorex process, a reduction of stage heights in extraction columns by factors of 2 to 4.⁴⁰

4.1 Acid Thorex Process

In the Acid Thorex process, both uranium and thorium are extracted from the fission-product-bearing nitric acid solution (Fig. 18). Protactinium-233, present at short cooling times, is not extracted. Aluminum is present (0.1 M) as a complexing agent for fluoride, added in the previous dissolution step, and is therefore not effective as a salting agent. The volume of the evaporated waste is a tenth that from the Interim 23 process. Decontamination factors obtained were 1000, 5000, 1000, and 10⁵, respectively, for ruthenium, zirconium-niobium, protactinium, and rare earths. Uranium and thorium losses were 0.01 and 0.3%, respectively. A high (30%) TBP concentration is required to extract both uranium and thorium, and, consequently, an acid-deficient feed is used to counteract the increased tendency for extraction of fission products. When an acid feed was used, decontamination was reduced by a factor greater than 10.⁴¹ The high decontamination achieved with the acid-deficient feed is attributed to the slow conversion of the ruthenium, zirconium-niobium, and protactinium from highly inextractable species present in acid-deficient systems to the highly extractable species formed in the acid sections of the column.

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Fig. 18. Acid Thorex process.

In laboratory countercurrent experiments, the fission products contacted the aqueous phase for approximately 20 min. In pulse columns this time would be reduced to about 8 min. The two scrub solutions shown in the flowsheet combine to form a 1 M HNO_3 scrub. They are added separately, however, with the low-acid scrub at the top of the column to minimize extraction of acid with the organic product. Thus, the thorium and uranium may be costripped in a single column with minimum aqueous volume and number of stages. If the thorium and uranium are recovered separately in partitioning and strip columns, a single 1 M HNO_3 , 0.01 M PO_4^{3-} , 0.01 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ scrub solution at a relative flow rate of 1.3 is satisfactory.

4.2 Acid Interim 23 Process

An Acid Interim 23 process was developed³⁷ to extract U^{233} and leave the thorium with the fission products (Fig. 19). Protactinium-233, present at short cooling times, also remains with the fission products. After the Pa^{233} has decayed to U^{233} , the wastes can be re-extracted by the same process to recover the U^{233} (and thorium, if desired, using the Acid Thorex process). The flowsheet shows the use of 5% TBP to illustrate a high processing rate. This is close to the maximum rate, since third-phase formation occurred with 10% TBP. In equipment in which criticality is not controlled by geometry, 2.5% TBP is used to limit the U^{233} concentration in the organic phase. Uranium loss was less than 0.01%, and the gross decontamination factor was approximately 10^5 . Advantages of the Interim 23 process include (1) rapid recovery of U^{233} and resultant low inventory charge and (2) high processing rate. Principal disadvantages are the necessity of processing the fission product and organic-degradation-product-bearing waste solution a second time to recover Pa^{233} and the relatively large waste volume.

4.3 Kilorod Program

A solvent extraction flowsheet was developed⁴² for purifying recovered U^{233} to be used in the fabrication of fuel elements by the Sol-Gel process⁴³ (Fig. 20). In laboratory countercurrent batch extraction experiments, the uranium was decontaminated from Th^{228} by a factor of greater than 10^4 . Di-sec-butyl phenyl phosphonate (DSBPP) is used rather than TBP because the separation factors for U/Th are

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Fig. 19. Acid Interim-23 process.

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Fig. 20. Kilorod Interim-23 process.

higher by a factor of 4 in the DSBPP system at thorium concentrations less than 100 g/liter.^{44,45,46} The increase in separation occurs principally in the scrub section of the column. The acid deficient aluminum nitrate scrub produces a low acidity product, with a nitrate-to-uranium ratio of 2.18 as required by the Sol-Gel fuel preparation process which follows in the Kilorod Program. Decontamination from Th^{228} and its' daughters is approximately 10^4 . Since DSBPP is not soluble in dodecane, an aromatic diluent, diethylbenzene (DEB) is used. The DSBPP in DEB is not as stable to chemical degradation as TBP in n-dodecane. When DSBPP in DEB was stirred 16 hr with nonradioactive feed and then used in a laboratory experiment, the distribution coefficient of uranium in the scrub section decreased by a factor of about 2. Decontamination from Th^{228} , however, was unaffected.

This separation of uranium from the daughters of U^{232} provides a product which can be handled in the semiremote, Sol-Gel vibratory-compaction equipment for at least ten days without overexposure to workers. The growth of activity in the product (Fig. 21) duplicates that predicted for the growth of the daughters of U^{232} in the natural activity of the U^{233} .⁴⁷

4.4 Protactinium Recovery Systems

The presence of relatively long half-life (27 days) Pa^{233} in short-decayed thorium reactor fuel, constitutes a major difficulty in the reprocessing of such fuel. Immediately after discharge from the reactor the protactinium is responsible for 90 to 99% of the beta-gamma activity and as much as 10% of the potential U^{233} in the fuel. With either the Interim 23 or the Acid Thorex flowsheet, the protactinium is hydrolyzed or precipitated in the acid feed solution and is not extracted with the solvent. Two processes being studied in the laboratory for possible recovery of the protactinium from short-decayed thorium fuel solutions are: (1) adsorption of protactinium from highly acidic dissolver solution on silica gel or on unfired powdered Vycor glass or (2) the coextraction of the protactinium with the thorium and uranium, using a Thorex-type solvent extraction flowsheet.

Solubility studies on Pa^{231} showed that protactinium remained homogeneously dispersed in solutions equivalent to those to be obtained in dissolution and feed of

Fig. 21. Growth of activity in U-233 following solvent extraction purification.

Consolidated Edison fuel irradiated to 20,000 Mwd/ton. The solutions contained 116 g/liter Th, approximately 0.07 g/liter Pa, 11 $\underline{\text{M}}$ HNO_3 , 0.1 $\underline{\text{M}}$ Al, less than 0.1 $\underline{\text{M}}$ F, and 40 g/liter Th, 0.09 g/liter Pa, 5 $\underline{\text{M}}$ HNO_3 , 1 $\underline{\text{M}}$ Al, approximately 0.1 $\underline{\text{M}}$ F. Such solutions showed no decrease in protactinium concentration after standing in a plastic container for a month at room temperature. These solutions also showed no change in concentration after contacting either welded or unwelded type 347 stainless steel coupons for one week at room temperature.⁴⁸ The solubilities are in agreement with the observations of Hardy et al.⁴⁹ that protactinium stock solutions containing 10^{-3} $\underline{\text{M}}$ Pa in 6 $\underline{\text{N}}$ HNO_3 were stable for many months.

Laboratory experiments demonstrated that at least 95% of the protactinium in the synthetic dissolver solution could be adsorbed on columns containing either unfired Vycor glass or laboratory-prepared silica gel.⁴⁸ When the experiments were terminated, the columns contained 5.0 and 3.2 mg of protactinium per gram of adsorbent, respectively. The amount of protactinium not adsorbed remained constant throughout the experiment. The protactinium was eluted at six times the feed concentration with 0.5 $\underline{\text{M}}$ oxalic acid. These laboratory experiments indicate that the protactinium in short-decayed thorium fuel may be adsorbed on radiation-stable inorganic materials directly from the dissolver solution. The decrease in activity of the thorium-uranium solution due to 95% removal of protactinium is equivalent to about a four-month decay of the fuel.

A low-decontamination "Acid Co-Extraction Process" is also being developed⁵⁰ for the recovery of protactinium in which protactinium, uranium, and thorium are simultaneously extracted from highly acid feed solutions with 30% TBP. In experiments with tracer protactinium, about 90% of it was extracted from 5 $\underline{\text{M}}$ HNO_3 --1 $\underline{\text{M}}$ $\text{Al}(\text{NO}_3)_3$, resulting in a decontamination factor of 70 from ruthenium and about 10^5 from rare earths. About half of the zirconium-niobium extracts with the product. A partitioning strip or a second solvent extraction cycle could be used to separate protactinium from uranium and thorium and to increase decontamination from fission products. Much of the zirconium-niobium will accompany the protactinium in this system, but additional decontamination is obtained by the decay of 65-day half-life Zr^{95} during the decay of the 27-day half-life Pa^{233} .

Either of these short decay processes results in the separation of protactinium, which will decay to U^{233} almost free of U^{232} . Such U^{233} is valuable for special uses.

5. CHOICE OF REPROCESSING METHOD

5.1 Thorium Fuel Processes

The choice of a processing method for the recovery of irradiated thorium fuels depends on which of the following objectives must be met: (1) short cooling times with immediate co-recovery of U^{233} , thorium, and protactinium vs long cooling for complete decay of Pa^{233} to U^{233} before recovery of U^{233} and thorium; or (2) short cooling time and recovery of U^{233} alone in a first cycle followed at a later time by recovery of additional U^{233} (and thorium, if desired) after complete decay of Pa^{233} . These considerations do not particularly affect the choice of fuel decladding or dissolution methods but seriously affect the choice of solvent extraction method. Items to be considered are: (1) solubility of protactinium in nitrate systems, (2) separation chemistry of protactinium in systems containing macro amounts of protactinium, (3) relative processing rates, and (4) volume of radioactive wastes. A summary of the extraction system variables taken from Figures 18 and 19 is given in Table 7.

The objective of recent solvent extraction development work has been to define these variables and thus obtain the data necessary for the choice of a processing method based on economics rather than chemical engineering limitations. For example, at present, short-cooled processes for direct extraction of Pa^{233} from nitrate systems could not be operated with guaranteed success since most development work on Pa^{233} recovery from nitrate solution has been done on a tracer scale. Experiments with macro amounts of Pa^{231} are in progress to confirm promising tracer-scale results. The solubility of protactinium appears to be sufficiently high in nitric acid Thorex dissolver solutions to warrant consideration of direct processing. At least 90% of the protactinium can be adsorbed directly from this solution on unfired Vycor or on silica gel. Thus the Acid Thorex process could be used for direct recovery of U^{233} and thorium in short-cooled processing after protactinium adsorption or after complete decay of Pa^{233} .

Table 7. Choice of Acid Extraction Process

Process	Cooling (days)	No. Cycles	Rate* (tonnes Th/day)	Waste Vol. (gal/tonne Th)
Interim 23	< 90	2, U	0.5	530
	> 120	1, U	1	530
Thorex	> 120	1, U and Th	0.5	53
Co-Ext. Thorex	< 90	1, U Pa and Th	0.2	~ 60

* For AEC conceptual plant; not applicable to plant optimized for thorium and uranium recycle processing.

but is not suitable for co-extraction of uranium, protactinium, and thorium since the protactinium is hydrolyzed in the acid-deficient feed. However, the low-decontamination Acid Co-Extraction process can probably be used to recover uranium, thorium, and protactinium simultaneously. The low decontamination factors for zirconium and niobium obtained in this process may not be significant since zirconium and niobium have low cross sections, and remote fuel fabrication is required in any event. The high-cross-section fission products are removed by factors of about 10^4 (see Sec 4.4).

The Interim 23 process, where only U^{233} is recovered, has a significant advantage over the Acid Thorex process in terms of maximum processing rate in a given set of critically safe equipment. With 5% TBP solvent, the thorium processing rate is 2 to 3 times that of the Acid Thorex process. But if the solvent concentration is limited to 2.5%, as is customary for criticality control, the processing rates are about the same.

The Acid Thorex process, where both uranium and thorium are recovered, has a distinct advantage over the Interim 23 process in terms of volume of high-level waste. Since the thorium remains in the aqueous raffinate with the fission products in the Interim 23 system, the evaporated waste volume is 10 times greater than for the Acid Thorex process.

Obviously, a final choice between the Interim 23 and Acid Thorex processes will depend on many variables. So long as thorium reactors are fueled with U^{235} and fresh

(unirradiated) thorium or U^{235} containing small amounts of recycled U^{233} and U^{232} and fresh thorium, direct fuel fabrication with minimal shielding is possible. In this case, the Interim 23 process will probably be preferable because of its potential quick recovery of U^{233} for short cooling times, and hence, low fuel amortization costs. However, when reactors are fueled with U^{233} , complete remote fuel fabrication will be required with either fresh or recycled thorium, and the Acid Thorex or Acid Co-Extraction processes may be preferable. Calculations by E. D. Arnold show that the specific activity of infinitely recycled thorium and infinitely recycled uranium will be approximately equal and hence that the shielding required for fabrication of U^{233} -thorium fuels will be increased by only 20% if recycled thorium is used. A complete re-evaluation of fuel cycle economics will be required when U^{233} fuels are to be fabricated and the additional results are available from the new technology now under development.

5.2 Processing Costs

A brief survey of the costs of recovery processes for irradiated thorium-uranium fuel was made with the assistance of A. D. Ryon, E. L. Nicholson, J. O. Blomeke and J. J. Perona (Table 8). For comparison purposes Acid Interim-23 (Fig. 18) and Acid Thorex (Fig. 19) flowsheets were drawn which use the same feed solution and represent nearly maximum throughput. The total volumetric capacities of the extraction columns were estimated by A. D. Ryon as 900 and 600 g/hr.ft² for the Acid Thorex and Acid Interim-23 flowsheets, respectively. This indicates Acid Interim 23 thorium capacity for thorium extraction 2.03 times greater than Thorex for a given column size. An evaluation of thorium processing in the conceptual AEC multipurpose fuel processing plant by E. L. Nicholson indicated that the plant capacity would be governed by the solvent system and that the Interim 23 process would have a capacity twice that for Thorex and that the difference in the cost of the fuel processing is not significant (Table 8). However, in this case the system is optimized for uranium recovery with the Purex process. A comparison of two plants with equal thorium processing capacity and optimized for the Acid Thorex or Acid Interim 23 processes showed an insignificant increase in capital and operating costs for the Acid Thorex process. The increase results

Table 8. Comparative Overall Cost of Acid Interim 23 and Thorex Processes in the AEC Conceptual Plant⁵¹

Either process will recover U²³³, which, based on 5% fuel, will be valued at \$750,000 (50 kg U²³³ at \$15 per gram in each tonne of thorium)

	Dollars per Metric Tonne Thorium	
	Acid Interim 23	Acid Thorex
Fuel Processing ^a	16,500	33,000
Waste Management ^b	9,500	1,900
	<hr/>	<hr/>
	26,000	34,900
Credit for Thorium ^c	---	11,000
	<hr/>	<hr/>
	26,000	23,900

^aBased on capacity for 1 tonne of thorium per day by the Interim 23 process, or 1/2 tonne per day by Thorex. Since it is optimized for uranium recovery by the Purex process it is not optimum for Thorex processing. Includes storage, head-end processing, solvent extraction, operation, utilities, amortization, etc., but not waste management.

^bSee Table 10.

^cBased on U. S. price of \$5 per lb thorium.

from amortization of larger solvent equipment required for the Acid Thorex process. Previous estimates⁵¹ have shown that the total cost of extraction equipment is only about 12% of the cost of the complete plant. Under these conditions the Thorex plant results in a much lower fuel processing cost (Table 9).

Estimates by J. O. Blomeke and J. J. Perona for management of the high-level wastes from Interim 23 and acidic Thorex processing were based on previous cost studies made for Purex and Thorex wastes⁵² (Table 10). Interim 23 processing is assumed in the first case with thorium remaining in the waste through final disposal. In the second case, recovery of thorium from Acid Interim 23 raffinate after 12 years of storage is assumed. Cost of the reprocessing of the solution for thorium recovery is not included.

The value of the thorium is assumed to pay for its recovery cost. The third case is for Acid Thorex. The raffinate volumes and compositions given in Figs. 18 and 19 were used as a basis for comparison. In all cases, the wastes were assumed to be evaporated, stored 12 years as liquids, converted to solids by pot calcination, stored for 18 years as solids in water-filled canals, shipped 1000 miles to a salt mine, and finally, disposed of permanently by burial in salt mines.

Both acid flowsheets being compared are at about the same level of development; they have resulted in excellent operation in laboratory equipment using tracer solutions but have not been evaluated at full-activity levels or in engineering equipment. Neither is sufficiently different from previously demonstrated processes (other than the chemistry of protactinium) that major operational difficulties would be expected.

Table 9. Comparative Overall Cost of Acid Interim 23 and Thorex Processes in Equipment Designed for Optimized Flowsheets^a

	Dollars per Metric Tonne Thorium	
	Acid Interim 23	Acid Thorex
Fuel Processing	16,500	18,500 ^b
Waste Management	9,500	1,900
	<hr/> 26,000	<hr/> 20,400
Credit for Thorium	---	11,000
	<hr/> 26,000	<hr/> 9,400

^aSame basis as for Table 8.

^b Allowances for solvent extraction equipment (12% of total charges) have been doubled to give a generous allowance for plant modifications.

Table 10. Waste Management Costs for Interim 23 and Acid Thorex Processes

	Cost (Dollars per tonne Thorium)		
	Acid Interim 23	Acid Interim 23 and Th Recovery	Acid Thorex
1. Raffinate evap	80	80	360
2. 12-yr interim liq storage	1940	1940	330
3. Raffinate evap	---	360	---
4. Reduction to solids	3210	520	520
5. 18-yr interim solids storage	3030	175	175
6. 1000-mile shipment	720	65	65
7. Disposal in salt mine	565	450	450
Totals	\$9500	\$3600	\$1900

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