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## AQUEOUS PROCESSING OF THORIUM FUELS, PART II

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AQUEOUS PROCESSING OF THORIUM FUELS, PART II

R. E. Blanco, L. M. Ferris, C. D. Watson, R. H. Rainey

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Gatlinburg, Tennessee, December 5-7, 1962.

ABSTRACT

The status of aqueous processing methods for thorium fuels is reviewed. A specially designed 320 ton shear was successfully tested for chopping full size simulated Consolidated Edison type unirradiated assemblies into 0.25-1.5 inch lengths. Pieces about 0.5-inch long are preferred since the core pellets are more severely crushed during the chopping operation, and consequently, the rate of core dissolution is enhanced. 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 engineering 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  $\sim 0.3\%$  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 dissolution of the ash in nitric acid or by grinding to  $\sim 200$  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-secbutyl phenyl phosphonate as the solvent. The "Acid" processes use nitric acid rather than aluminum as the salting agent.

## 1.0 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 was presented at the CNEN Symposium on Thorium Fuel Cycle at Rome in 1961.<sup>1</sup> This survey included aqueous decladding methods, core dissolution and solvent extraction studies, corrosion data and design criteria. The present paper presents recent work on mechanical decladding and core leaching techniques, dissolution of graphite and carbide type fuels, advanced solvent extraction techniques, and, 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, e.g. short cooled processing where protactinium is a problem vs 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 mechanical processing development work was carried out on a large engineering scale with a 250 ton shear using mock stainless steel assemblies with  $\text{UO}_2$ ,  $\text{ThO}_2\text{-UO}_2$ , or ceramic cores to simulate fuels in the mechanical decladding development program. Cladding dissolution studies with unirradiated  $\text{ThO}_2\text{-UO}_2$  fuels were also performed on an engineering scale but the core dissolution and extraction studies were confined to a laboratory scale using small irradiated fuel pins or tracer levels of activity.

## 2.0 MECHANICAL PROCESSING

Mechanical decladding<sup>2,3</sup> and shear leach<sup>6,11</sup> techniques for processing stainless steel clad uranium-thorium metal or oxide fuels have been successfully developed and tested on a small pilot plant scale. Mechanical decladding was used to remove the stainless steel cladding from irradiated sodium bonded uranium metal Sodium Reactor Experiment Fuel (SRE, Core 1). A similar technique could be used to declad the SRE Core 2 fuel (7.8% Th-U). An engineering-scale shear-leach complex was successfully tested using a 250 ton shear and a countercurrent leacher with prototype stainless steel clad ceramic,  $UO_2$ , and  $ThO_2-UO_2$  assemblies. Nuclear Fuel Services will use a similar system in a commercial fuel processing plant.<sup>4</sup> A conceptual study for installation of a shear-leach complex at the Idaho Chemical Processing Plant was completed.<sup>5</sup> Advantages of mechanical processing include: (1) lower waste disposal costs than for aqueous decladding. In a comparative cost estimate, waste costs were 8 times lower for mechanically decladding<sup>2</sup> SRE Core 1 fuel and 20 times lower for shearing and leaching<sup>6</sup> Merchant Ship Savannah fuel as compared to dissolution of the stainless steel cladding in sulfuric acid (Sulfex Process); (2) reduction of explosion hazard by removing liquid metal bonds prior to aqueous fuel dissolution; and (3) shattering of  $UO_2$  or  $ThO_2-UO_2$  fuel cores during shearing, which increases the core dissolution rate 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 designed<sup>2</sup> equipment complex (Fig. 1) using the steps shown in Fig. 2. The SRE Core 1 fuel consists of clusters, 105.5-in. long, of 7 elements or rods containing

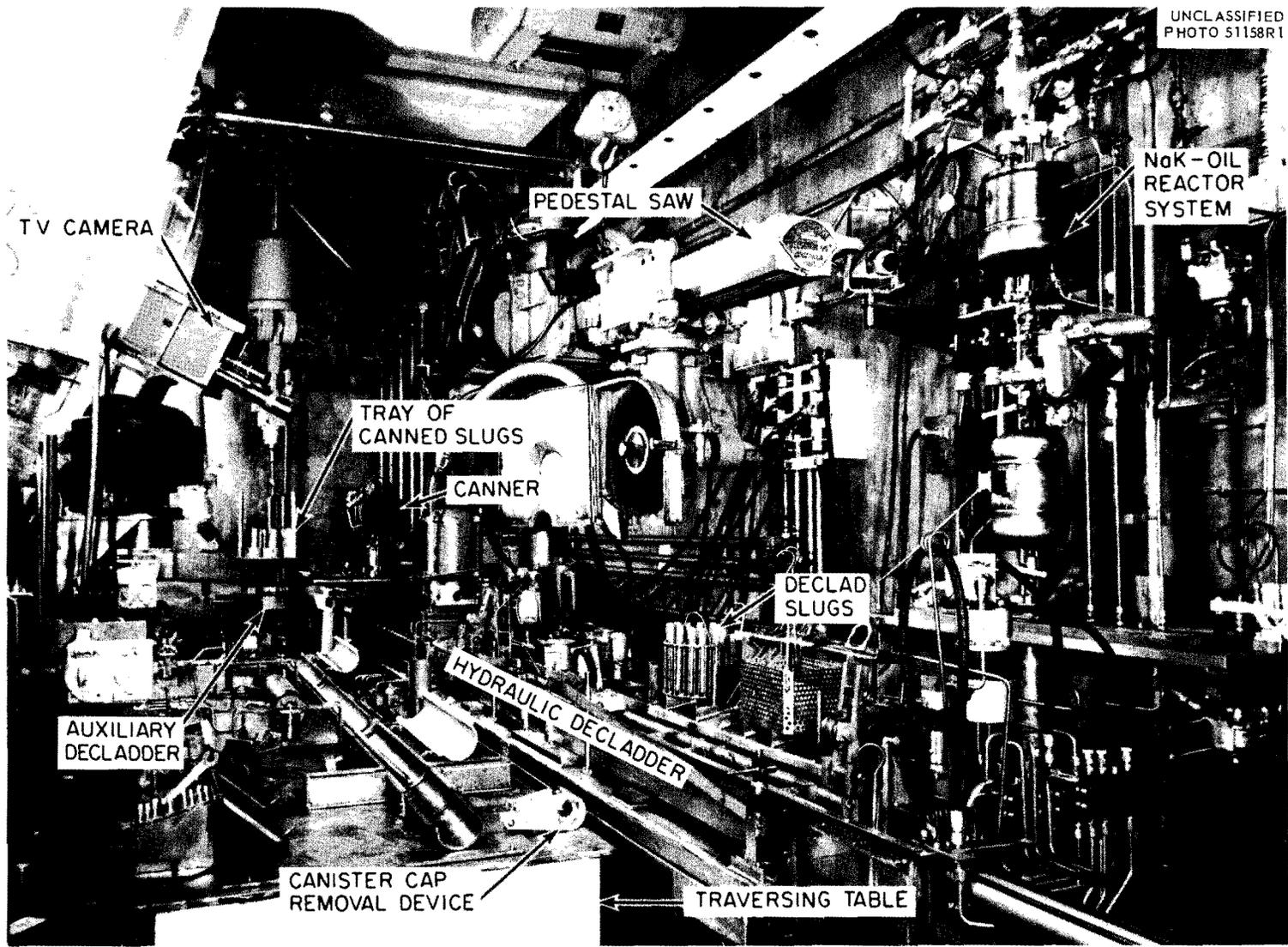


Fig. 1. Mechanical processing equipment for decladding SRE Core I fuel (interior view, Cell A) ORNL segmenting facility.

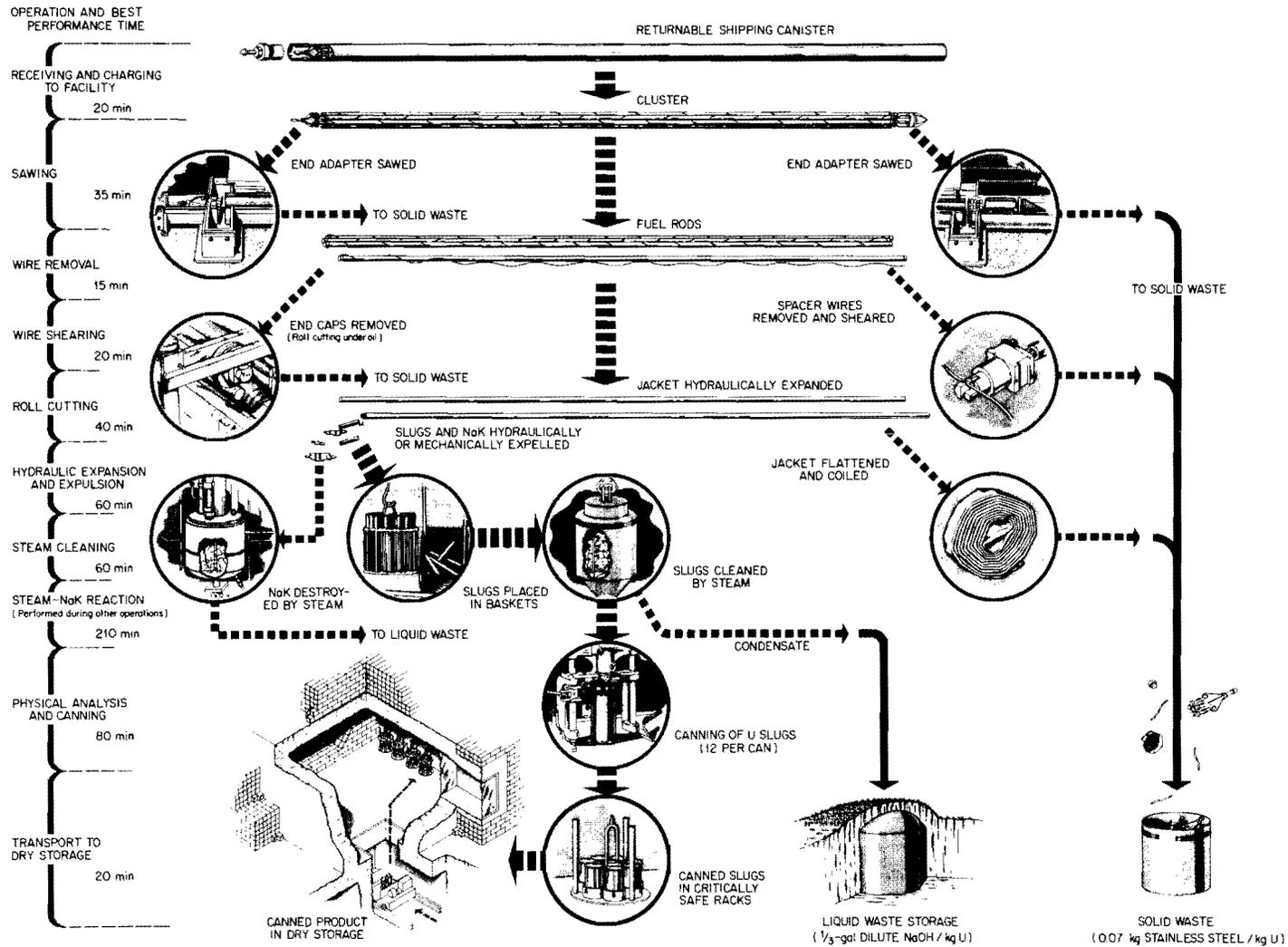


Fig. 2. Mechanical decladding of SRE fuel.

2.7 percent enriched uranium slugs in thin walled, 0.010 in., 304 stainless steel tubular cladding, 92-5/16-in. long by 0.790-in.-o.d. The active fuel length is 72 in. consisting of 12 slugs, 0.750-in.-dia by 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 expansion of the NaK bond and serves as a reservoir for fission gases. The fuel was irradiated to 675 Mwd/tonne and decayed 2 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.<sup>7,9</sup> Undesirable fuel characteristics, such as 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 kg U/hr to 9.2 kg U/hr with negligible loss of uranium and plutonium. Hydraulic expansion of the clad and expulsion of the slugs, the primary method of decladding, was effective on 16% of the rods. Slugs from 77% were physically 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 manual peeling of the clad from each fuel slug with a manipulator. The primary and secondary methods could not adequately cope with the damaged fuel. Manipulator decladding 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),<sup>7</sup>

could be decladded mechanically if the fuel is not damaged and 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.<sup>10</sup> A greater than stoichiometric amount of carbon in the fuel causes embrittlement of the cladding.

## 2.2 Shear-Leach

The experimental chop-leach complex (Figures 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, or Rural Cooperative reactors or any subassembly whose cross section does not exceed 6.36 in. x 6.36 in. ORNL prototype assemblies, stainless steel clad ceramic,  $\text{ThO}_2$ , or  $\text{UO}_2$ , 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  $\text{UO}_2$  were sheared and leached at a rate of about 6.5 kg of  $\text{UO}_2$ /hr. The cost of the shear was \$185,000 and the conveyor feeder and leacher were \$40,000 each. Tests in which stainless clad  $\text{UO}_2$ - $\text{ThO}_2$  fuel prototype assemblies were sheared into 1/2 in. and 1 in. lengths were satisfactory, and combined shear-leach tests on unirradiated stainless steel clad  $\text{ThO}_2$  and Zircaloy-2 clad  $\text{UO}_2$  is scheduled for early 1963. Irradiated fuel will not be processed.

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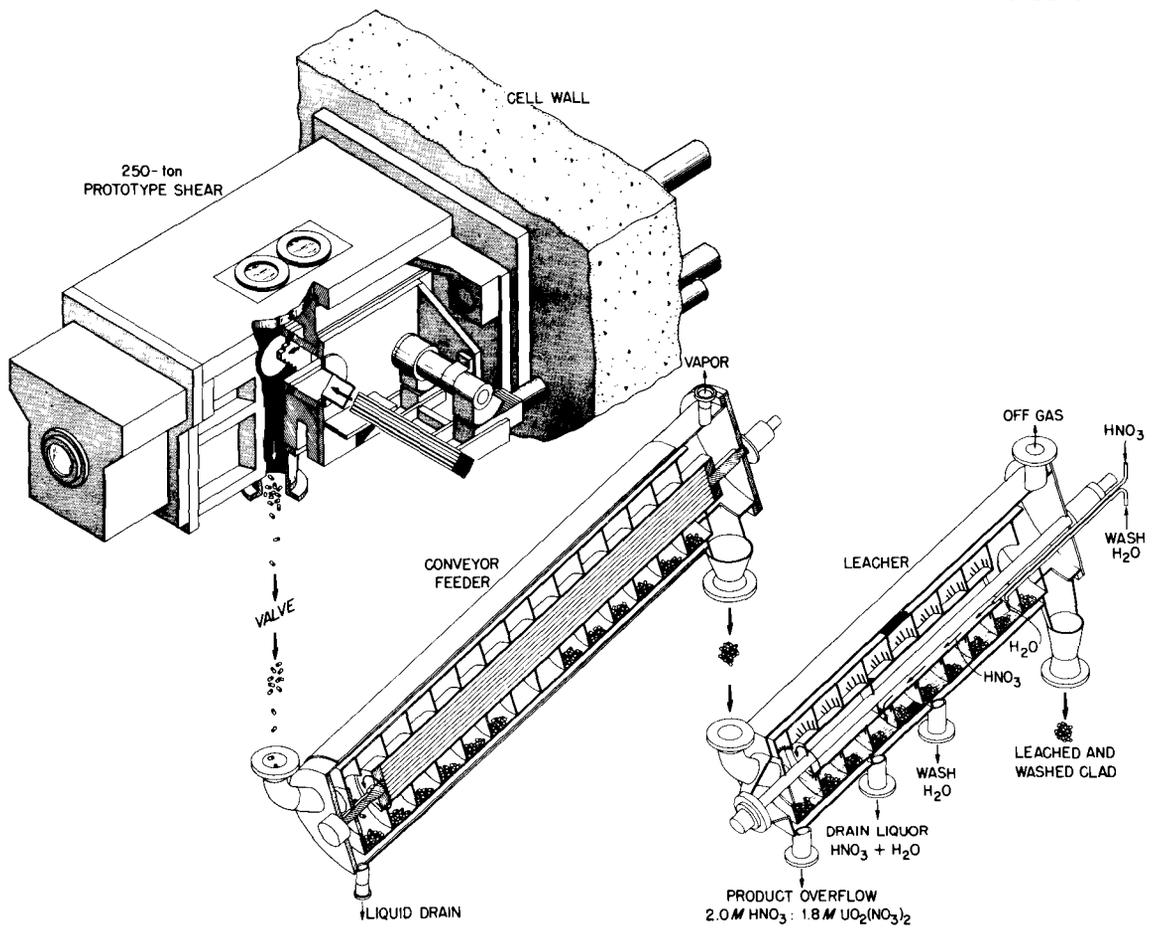


Fig. 3. Shear and leach complex.

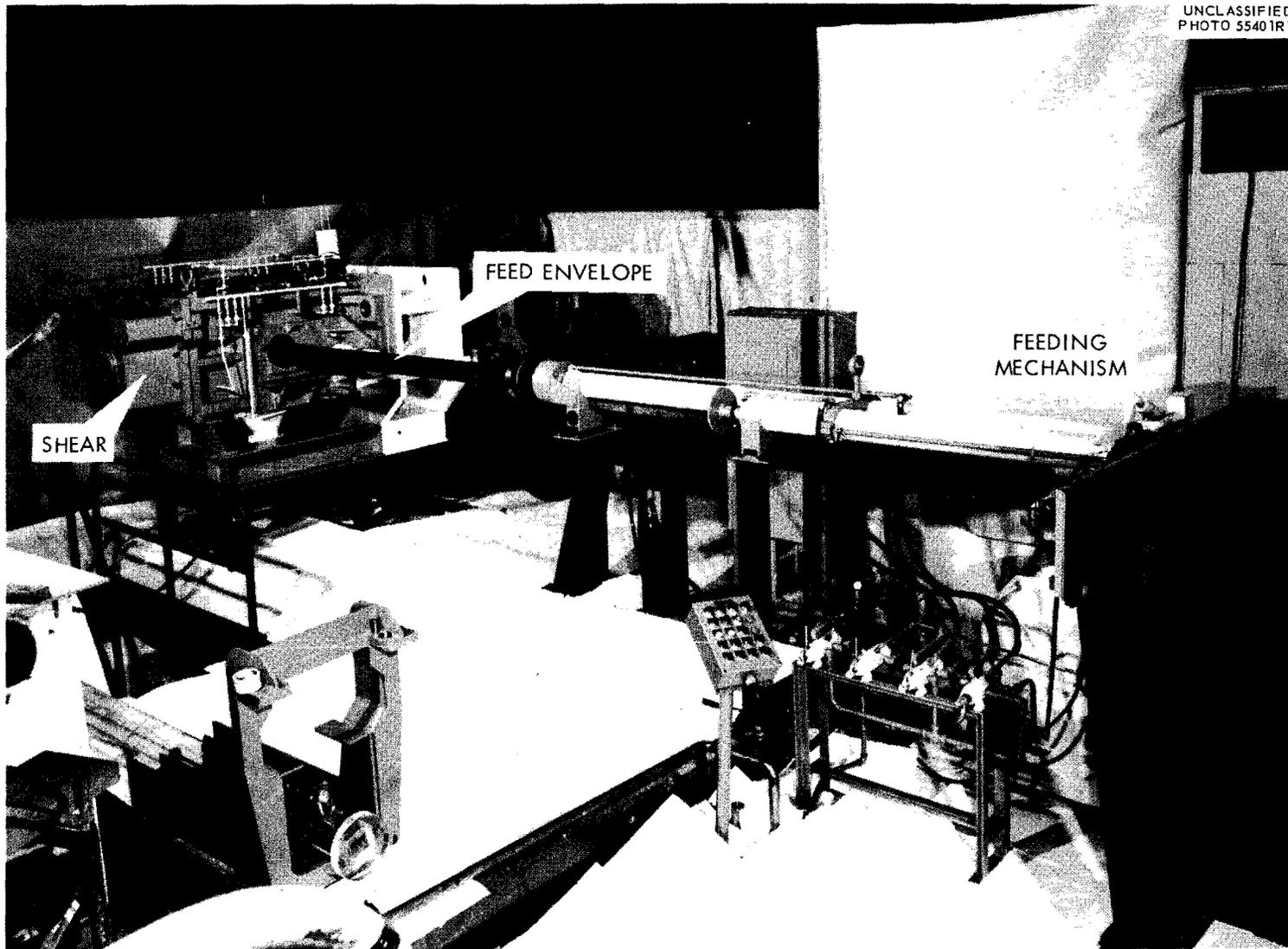


Fig. 4. ORNL 250 ton shear assembly.

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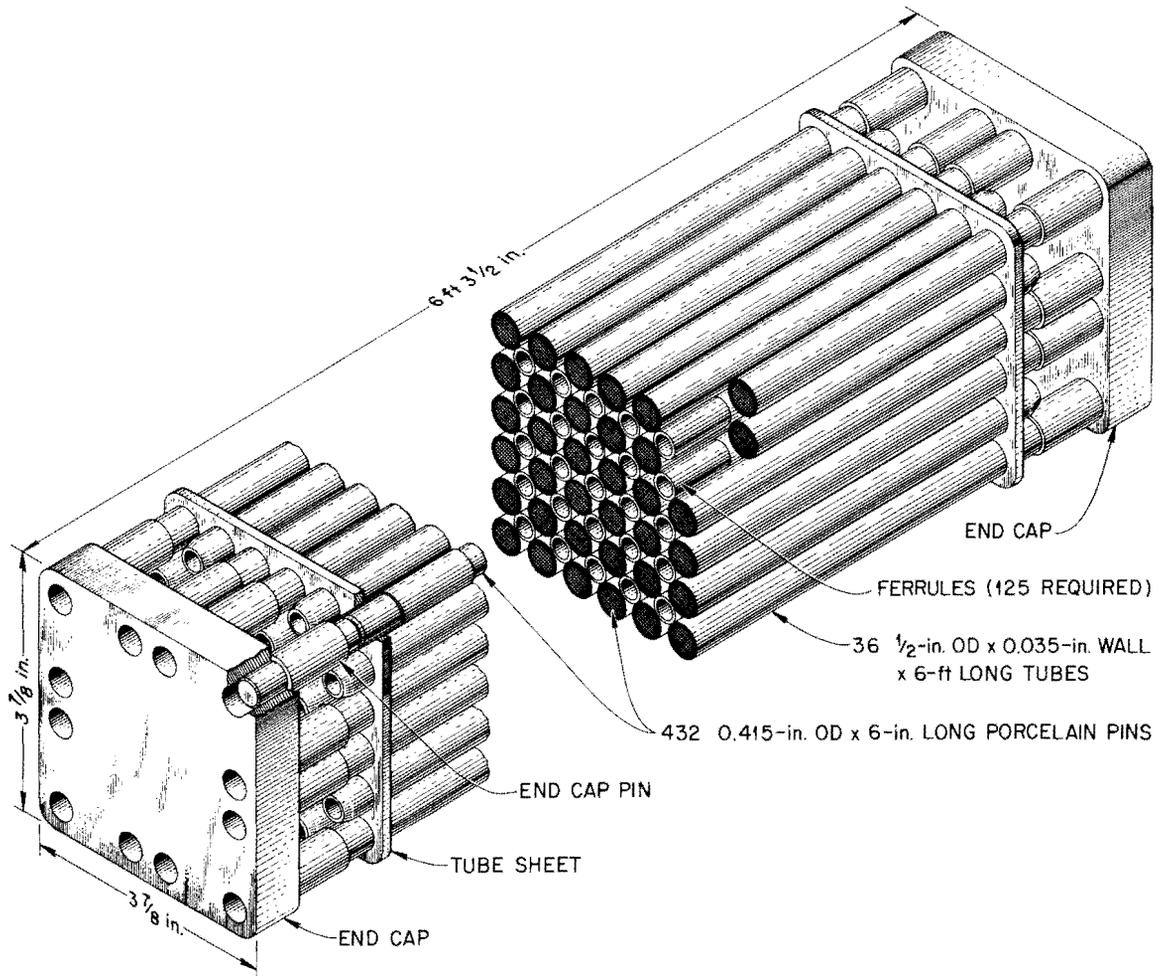


Fig. 5. Prototype fuel element Mark I.

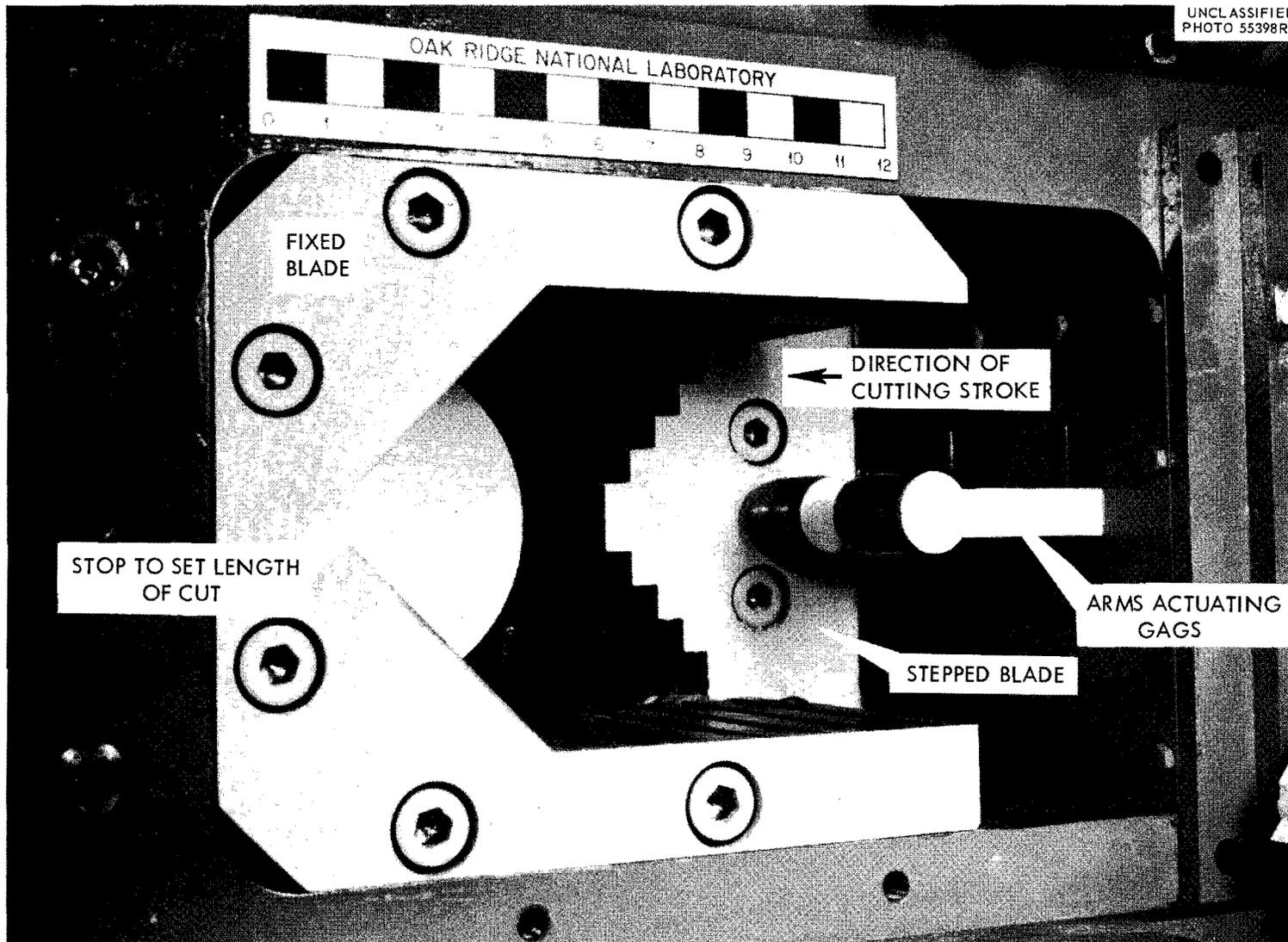
Shear. — The life of the stepped moving shear blade (Fig. 6) is estimated at 10,000 cuts of a 36 tube ORNL Mark I assembly filled with porcelain,  $UO_2$ , or  $UO_2-ThO_2$ . A Squarekeen\* No. 3 blade was chipped on the main tooth after 5982 cuts on porcelain filled ORNL Mark I prototype assemblies. 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 which can be held and sheared satisfactorily is 1.5 in. long, the width of the inner gag. A 1-in.-wide 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 using ferrules as spacers between fuel tubes are easily sheared. Unbrazed assemblies, using 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 is produced. These chunks cannot be handled in a continuous countercurrent leacher because they cannot be completely submerged in the counterflowing acid. Also, these chunks may block the flow of solids in a continuous leacher where dimensions are minimized because of criticality considerations.

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\* 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.



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

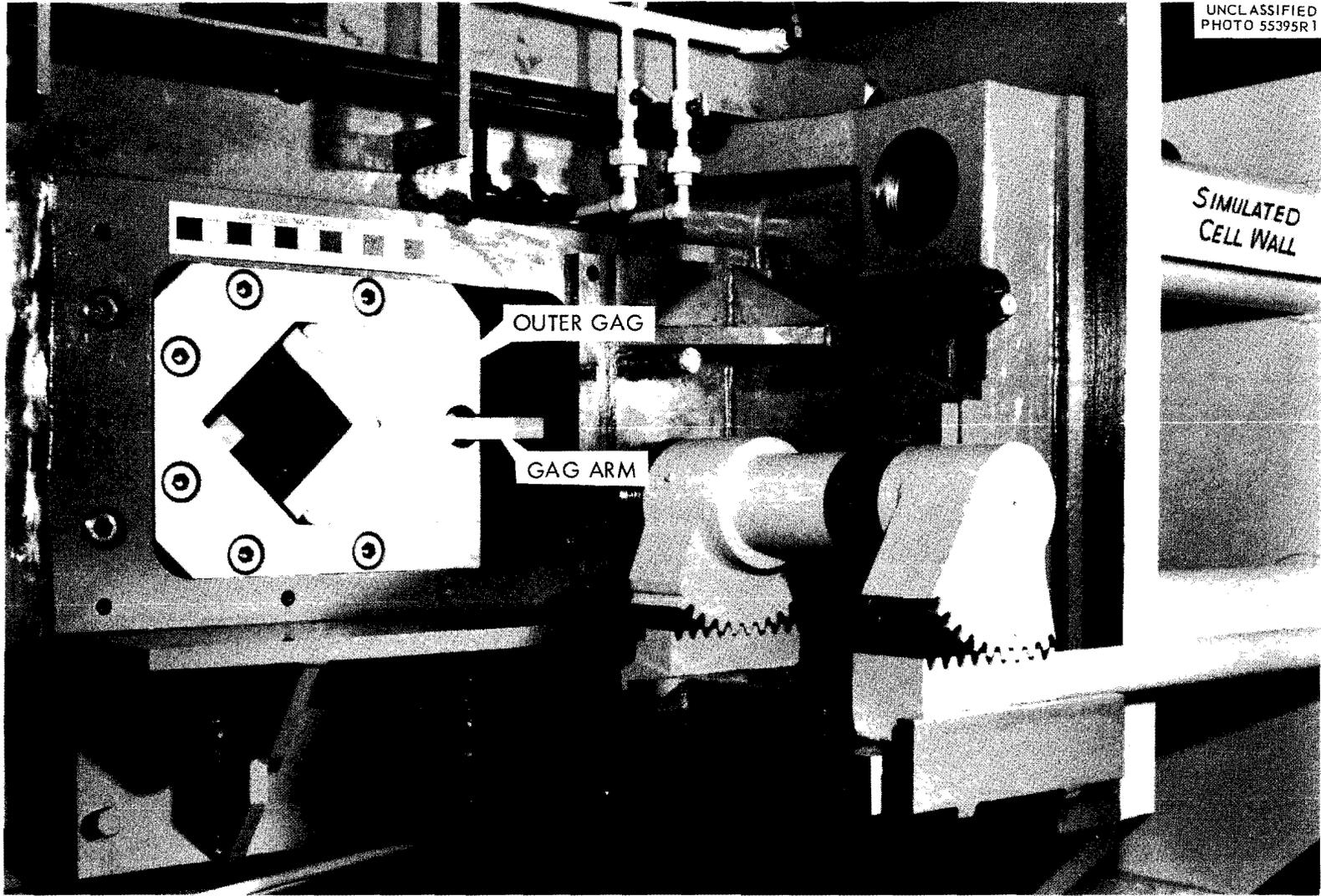
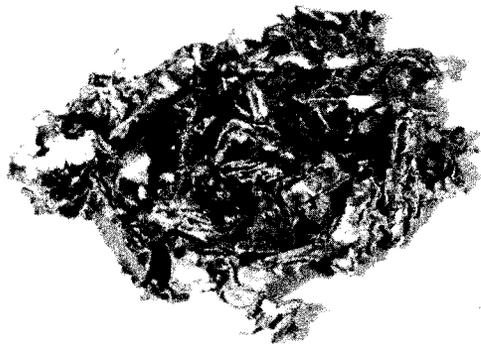
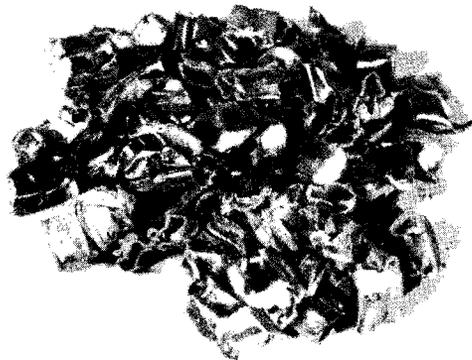


Fig. 7. Gag for ORNL 250 ton shear.

1/4-inch  
Sections



1/2-inch  
Sections



1-inch  
Sections

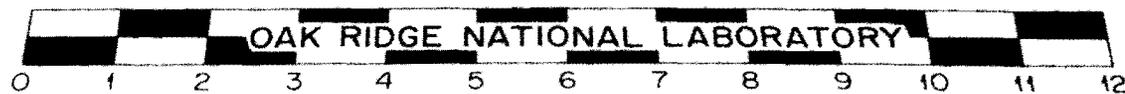


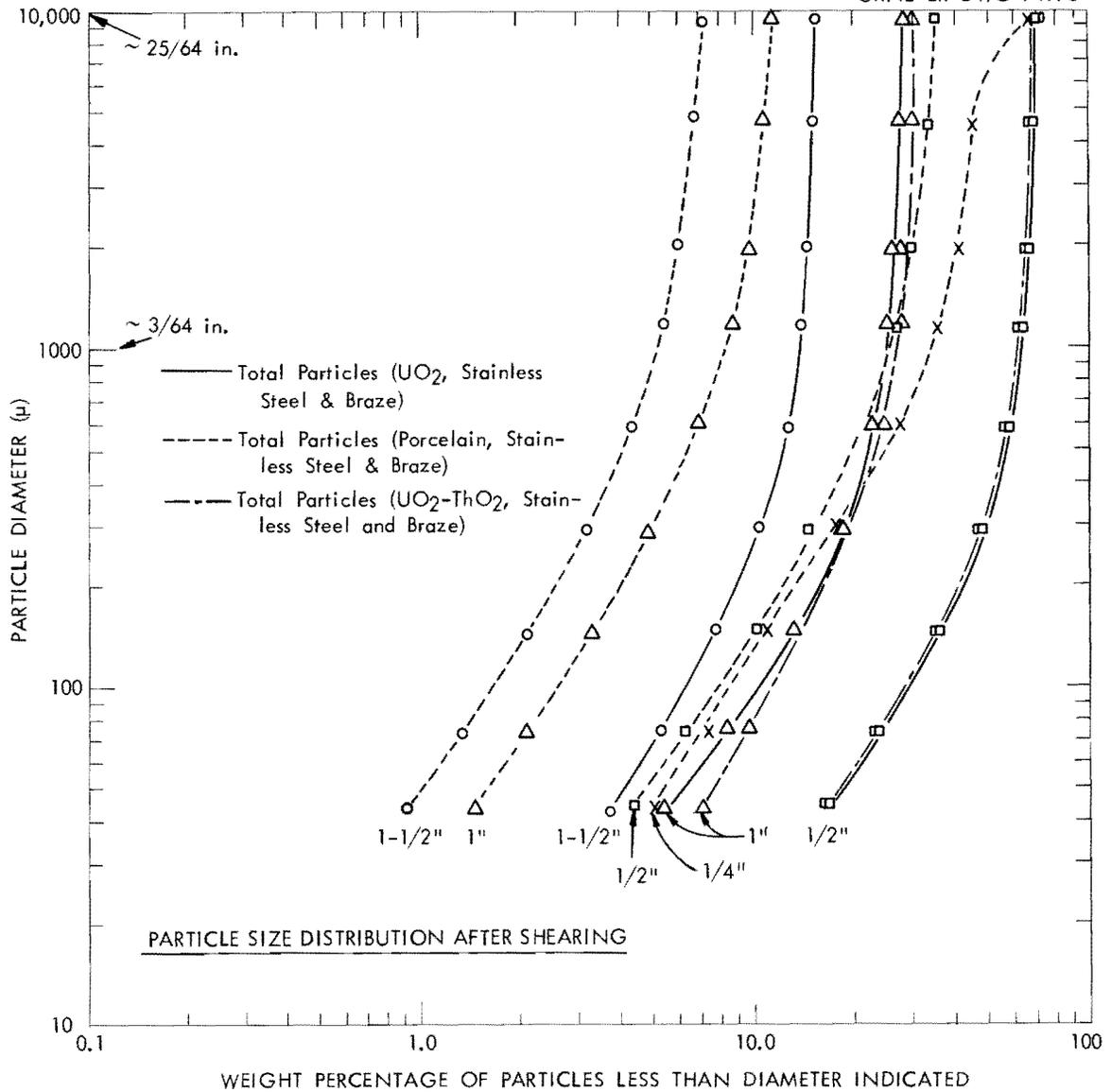
Fig. 8. Comparison of stainless steel tubing when shearing a porcelain-filled ORNL Mark I prototype fuel assembly into 1/4-, 1/2-, and 1-inch sections using a stepped blade and ORNL 250 ton shear. Dislodged porcelain fines are not shown.

A batch leacher may be required for fuels containing tube sheets. The size distribution of particulate composites composed of clad, core and braze metal which were dislodged during the shearing of (a) porcelain, (b)  $\text{UO}_2$ , and (c)  $\text{UO}_2$ - $\text{ThO}_2$  filled ORNL stainless jacketed prototype fuel into 1/4-in., 1/2-in., 1-in., and 1-1/2-in. lengths are presented in Figure 9. Curves of the particle size distribution of each component are available.<sup>11</sup> Generally, sheared  $\text{UO}_2$  filled and  $\text{UO}_2$ - $\text{ThO}_2$  filled assemblies produce equal quantities of particulates. The amount of  $\text{UO}_2$  and stainless steel dislodged increases as the length of sheared pieces is decreased (Table 1).

The cladding of a porcelain-filled Mark I assembly was carburized prior to shearing to simulate hardening and embrittlement of fuel cladding from neutron bombardment in a reactor. Carburization resulted in two effects: (a) more core and clad were dislodged, Table 2 and Figure 10, than from an untreated assembly, and (b) the tonnage required was only about one-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  $\text{UO}_2$  pellets irradiated to  $\sim 1600$  Mwd/ton U did not differ significantly from the amount produced from unirradiated specimens<sup>12</sup> ( $\sim 6\%$   $< 10$  mesh for 1 in. 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.

A bellows sealed flapper valve (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

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$$\text{Weight percentage} = \frac{\text{Weight of all particles dislodged (g)}}{\text{Weight of assembly (g)}} \times 100$$

Fig. 9. Distribution of total particles smaller than 9520  $\mu$  dislodged from the shearing of porcelain,  $\text{UO}_2$ , or  $\text{UO}_2\text{-ThO}_2$ -filled ORNL Mark I fuel into 1/4-, 1/2-, 1-, and 1-1/2-in. lengths.  
 Conditions: (1) Horizontally-actuated ORNL 250-ton shear; stepped blade operated at 1.22 in./sec, 4.2 cuts/min. (2) Description of fuel assembly sheared: square bundle (3.625 in. x 3.625 in.) of 36 tubes, 1/2 in. in OD x 72 in. long x 35 mils thick, with 1/4-in. OD x 1-in.-long Kanigen or Nicro-brazed spacer ferrules at a spacing of about 12-in. The tubes were filled with either  $\text{UO}_2$  or  $\text{UO}_2\text{-ThO}_2$  pellets, 0.420 in. x 0.625 in. long, or porcelain, 0.420 in. x 3 in. long.

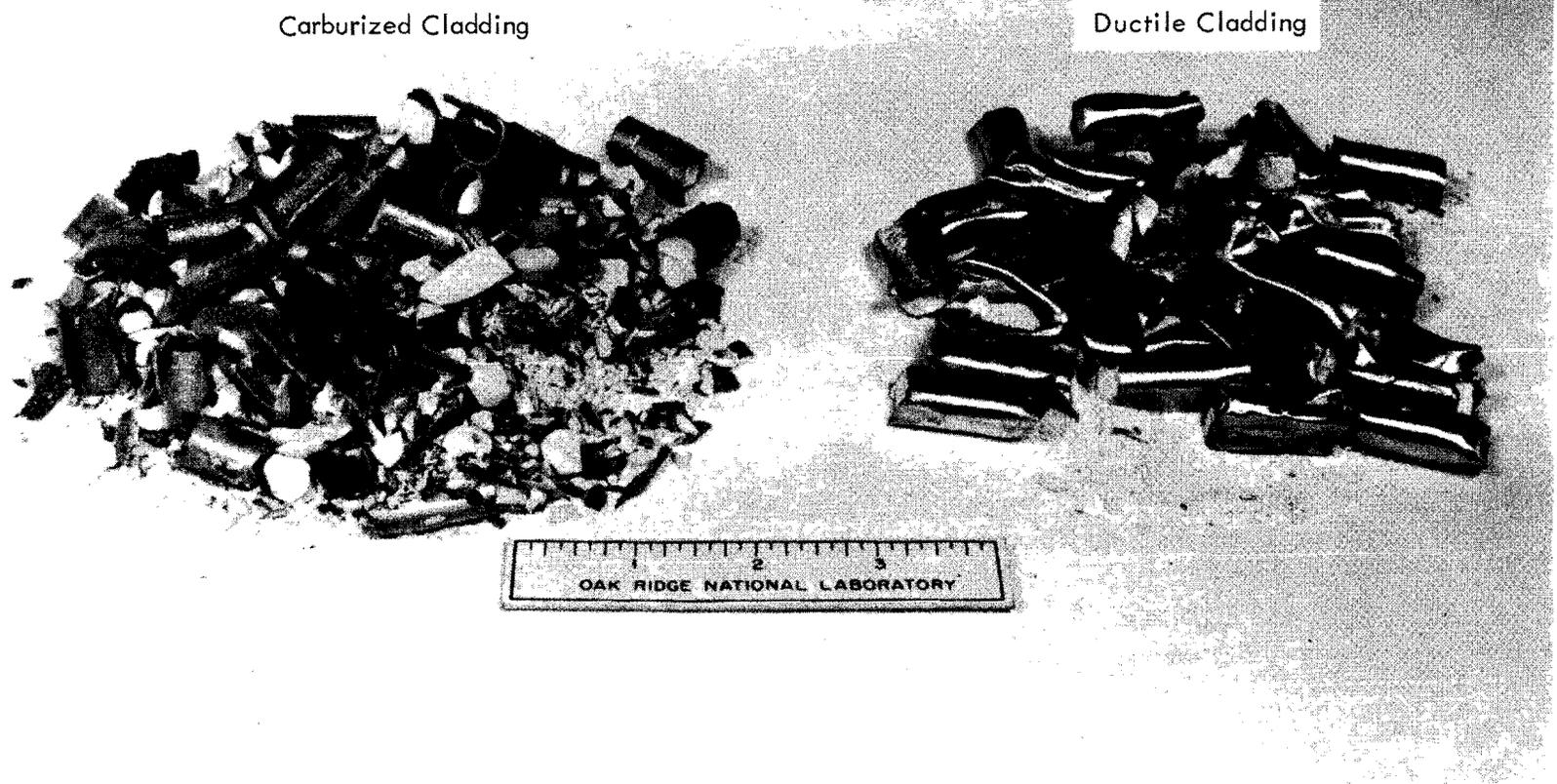


Fig. 10. Comparison of single cut made on carburized and ductile stainless steel clad porcelain filled ORNL Mark I prototype fuel assemblies.

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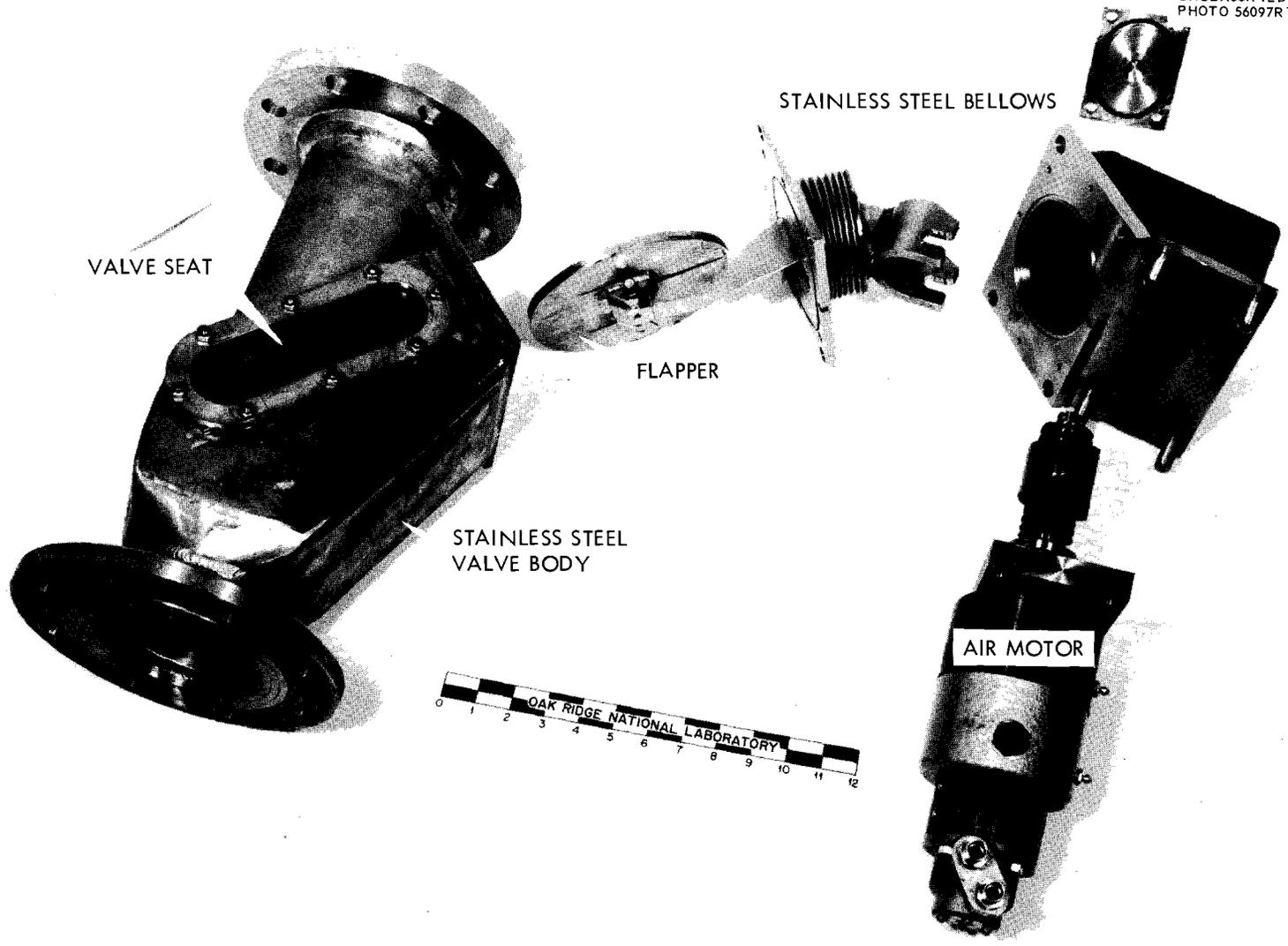


Fig. 11. Exploded view of bellows sealed flapper valve.

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TABLE 1

Distribution of UO<sub>2</sub> and Stainless Steel Particles from a Sheared ORNL Mark I Fuel Assembly

ORNL Mark I Assembly: square bundle, 3.625 in. x 3.625 in., of 36 stainless steel tubes 1/2 in. OD x 72 in. long x 35 mil wall, assembled with 1/4 in. OD x 1 in. long Kanigen or Nicro brazed spacer ferrules at ~ 12 in. spacing. Tubes filled with UO<sub>2</sub> pellets, 0.420 in. OD x 0.625 in. long.

Sheared Length (in.)	UO <sub>2</sub> , Wt % <sup>(1)</sup>			
	Dislodged			Retained in Clad
	<44 μ	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 % <sup>(2)</sup>			
	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

$$\text{Wt \% (1)} = \frac{\text{Weight (g) of UO}_2 \text{ Dislodged}}{\text{Weight (g) of UO}_2 \text{ in Fuel Assembly}} \times 100$$

$$\text{(2)} = \frac{\text{Weight (g) of Stainless Steel Dislodged}}{\text{Weight (g) of Stainless Steel in Fuel Assembly}} \times 100$$

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TABLE 2

Distribution of Particles from UO<sub>2</sub>, Porcelain, and Carburized Porcelain-Filled ORNL Mark I Fuel Assemblies Sheared into 1-in. Lengths

ORNL Mark I Assembly: square bundle (3.625 in. x 3.625 in.) of 36 stainless steel tubes 1/2 in. OD x 72 in. long x 35 mil wall, assembled with 1/4 in. OD x 1 in. long Kanigen or Nicro brazed spacer ferrules at ~ 12 in. spacing. Tubes filled with 0.420 in. OD x 3 in. long porcelain sections or UO<sub>2</sub> sections, 0.420 in. OD x 0.625 in. long.

Core Material	Core Material, Wt % <sup>(1)</sup>			Retained in Clad
	Dislodged			
	<44 μ	44-1,000 μ	1,000-9,520 μ	
UO <sub>2</sub> (Ductile Clad)	7.4	25.6	2.4	64.6
Porcelain (Ductile Clad)	3.0	16.2	4.3	76.5
Porcelain (Carburized Clad)	3.5	24.0	16.0	56.5
Core Material	Stainless Steel, Wt % <sup>(2)</sup>			Retained
	Dislodged			
UO <sub>2</sub> (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

$$\text{Wt \% (1)} = \frac{\text{Weight (g) of Core Material Dislodged}}{\text{Weight (g) of Core Material in Fuel Assembly}} \times 100$$

$$\text{(2)} = \frac{\text{Weight (g) of Stainless Steel Dislodged}}{\text{Weight (g) of Stainless Steel in Fuel Assembly}} \times 100$$

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 was estimated from tests<sup>13</sup> to be about 4 years, if used hourly.

Leaching. — In the shear-leach complex, sheared fuel is leached countercurrently 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 acid flowing through the weirs. Leaching takes place in the lower 4 stages of the spiral and washing of the leached clad occurs in the upper six stages. To insure submergence of sheared fuel under the acid dissolvent, the slip angle for 1.5, 2.25, and 3.0 liter batches of empty 304L stainless steel tubing (1-in.-long), solid stainless steel rod (1/2-in.-diam x 1-in.-long) and stainless steel jacketed porcelain filled Mark I sheared 1-in.-long were measured at leacher elevations of 10, 20, and 30 degrees. There was little difference in the slip angle of equal volumes of empty cladding, solid stainless steel rods and porcelain filled Mark I 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 I 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 feed end of leacher) sufficient to bring an originally horizontal batch to the point of slippage (Fig. 12). Slippage first occurs when approximately one half of the batch is above the liquid

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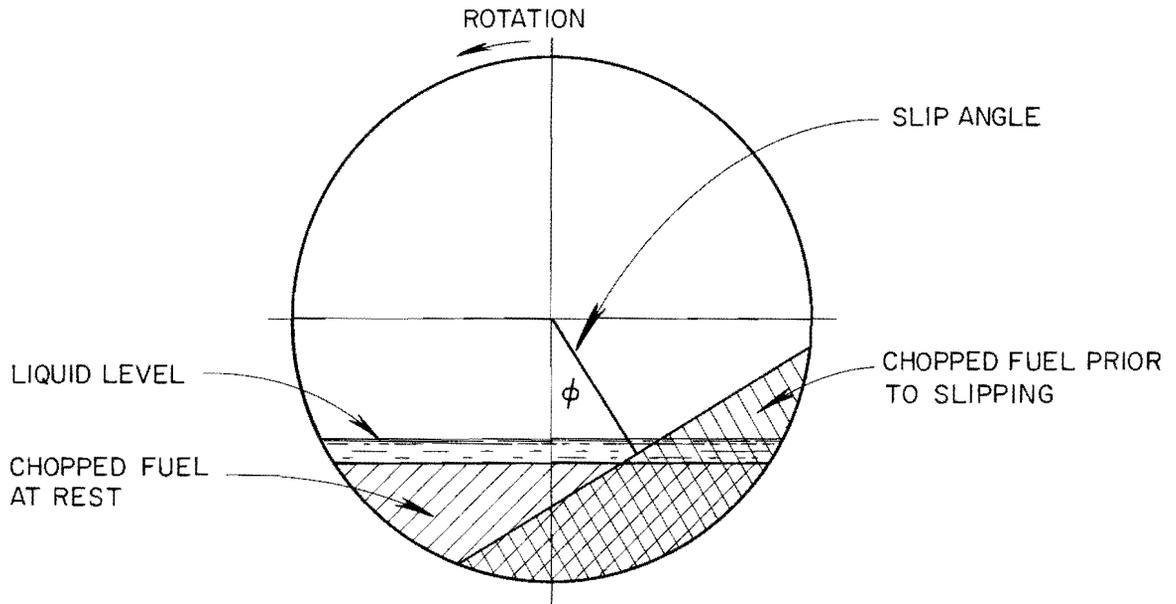


Fig. 12. Cross-section of leacher from feed end showing slip angle.

level. To insure submergence of chopped fuel as it is advanced each flight, the leacher is rotated 360° plus the slip angle (~28° for 2.25 liter batch) then reversed by the amount of the slip angle.

Leaching of unirradiated UO<sub>2</sub>-filled ORNL Mark I prototype fuel sheared into 1/2-in., 1-in., 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<sub>3</sub> fed at a rate of 4 g moles HNO<sub>3</sub>/g mole UO<sub>2</sub>. At this acid strength and ratio, apparent steady state was attained at about the 5th hour. For all sheared lengths tried, a growing inventory of UO<sub>2</sub> was recorded (Figure 14). Increasing the acid to UO<sub>2</sub> ratio from 4 to 6 eliminated the UO<sub>2</sub> inventory after the 3rd hour. Mixed ThO<sub>2</sub>-UO<sub>2</sub> 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<sup>14,15</sup> (Sec. 3.1.5), a residence time of 10-15 hr should be adequate for the continuous leacher.

### 3.0 AQUEOUS DISSOLUTION METHODS

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

Fuel claddings can be dissolved in a suitable reagent prior to dissolution of the oxide core in boiling 13 M HNO<sub>3</sub>-0.04 M HF.<sup>14,16-28</sup> 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<sup>16-19,21</sup> the stainless steel cladding is dissolved in boiling dilute sulfuric acid whereas the cladding is dissolved in dilute aqua-regia in the Darex process.<sup>16-18,20,22</sup> Hot-cell experiments<sup>14,23</sup> have shown that the Sulfex process will probably be satisfactory for highly irradiated

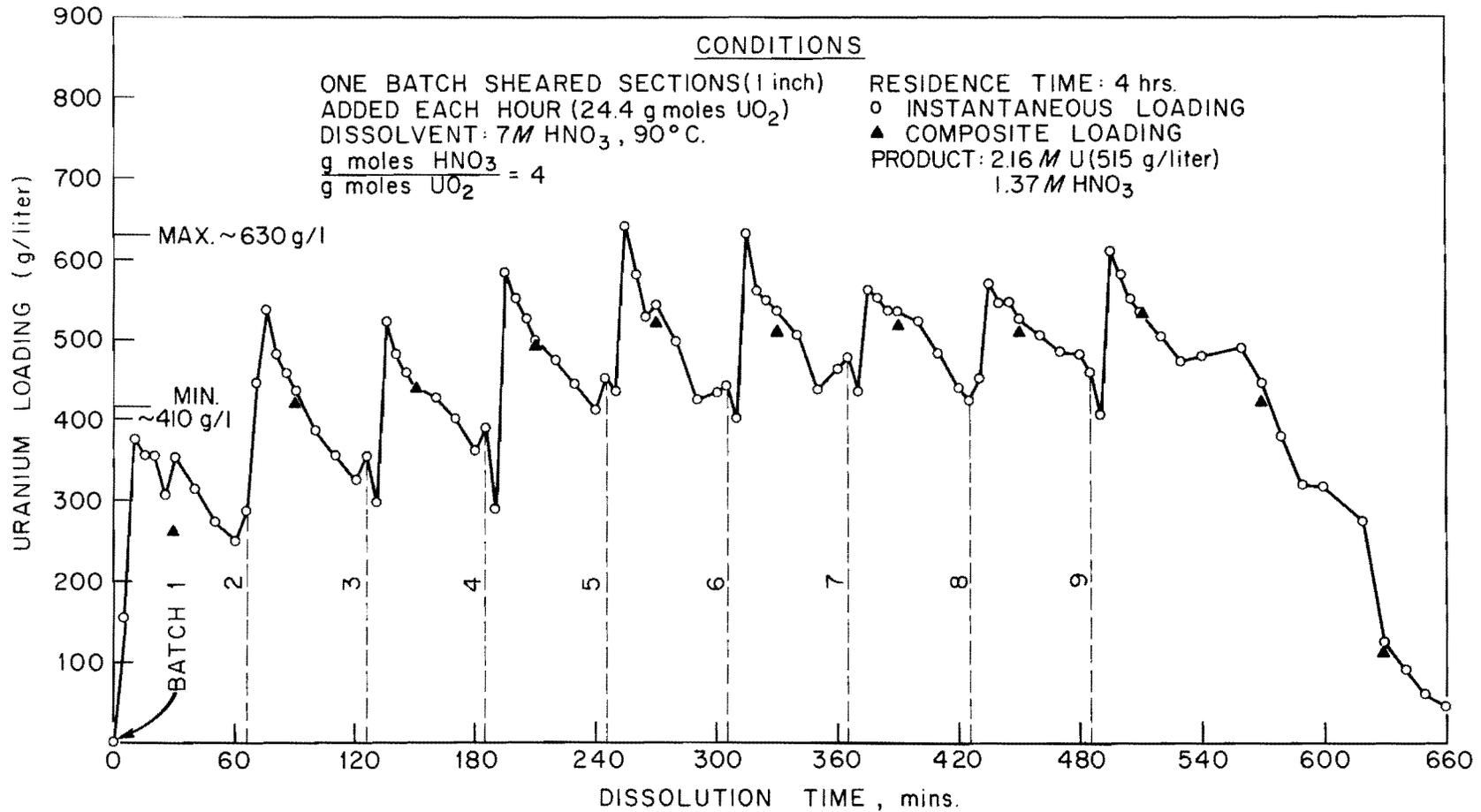


Fig. 13. Uranium loading as a function of dissolution time for a 4 stage rotary leacher.

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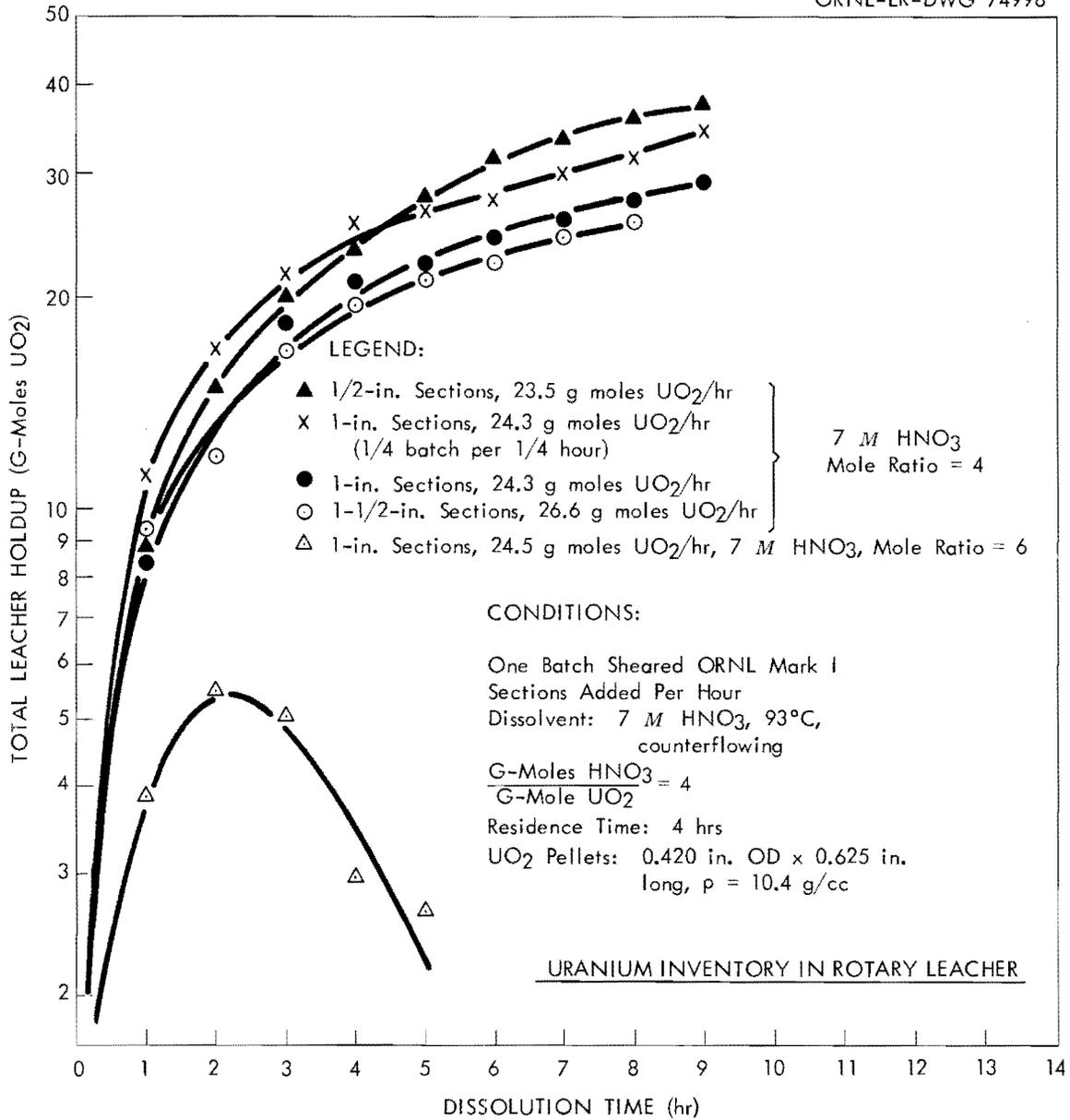


Fig. 14. Uranium inventory in rotary leacher versus dissolution time.

elements, but that losses of uranium to the decladding solution are excessive with the Darex system. The BORAX-IV core was processed<sup>29</sup> at the Idaho Chemical Processing Plant (ICPP) using a process<sup>28</sup> which involved dissolution of the aluminum cladding in NaOH-NaNO<sub>3</sub>, dissolution of the lead bond in dilute nitric acid, and dissolution of the ThO<sub>2</sub>-UO<sub>2</sub> core in 13 M HNO<sub>3</sub>-0.04 M NaF.

### 3.1.1 Dissolution of Stainless Steel Cladding in Sulfuric Acid

In the Sulfex process for CETR fuel<sup>16-19,21</sup> (Fig. 15), the 30-mil stainless steel cladding is dissolved in three times the stoichiometric amount of boiling 4 to 6 M H<sub>2</sub>SO<sub>4</sub> in 1 to 3 hr. About 1.1 moles of hydrogen off-gas are evolved when 55 grams (1 mole) of stainless steel is dissolved. The stainless steel cladding is often passive from either a protective oxide film or from traces of nitric acid in 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.<sup>14,23</sup> 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 ThO<sub>2</sub>-UO<sub>2</sub> reactor fuels.

### 3.1.2 Darex Decladding

In the Darex process for CETR fuel<sup>16-18,20,22</sup> (Fig. 16), the stainless steel cladding is dissolved in sufficient boiling 5 M HNO<sub>3</sub>-2 M HCl to yield a solution

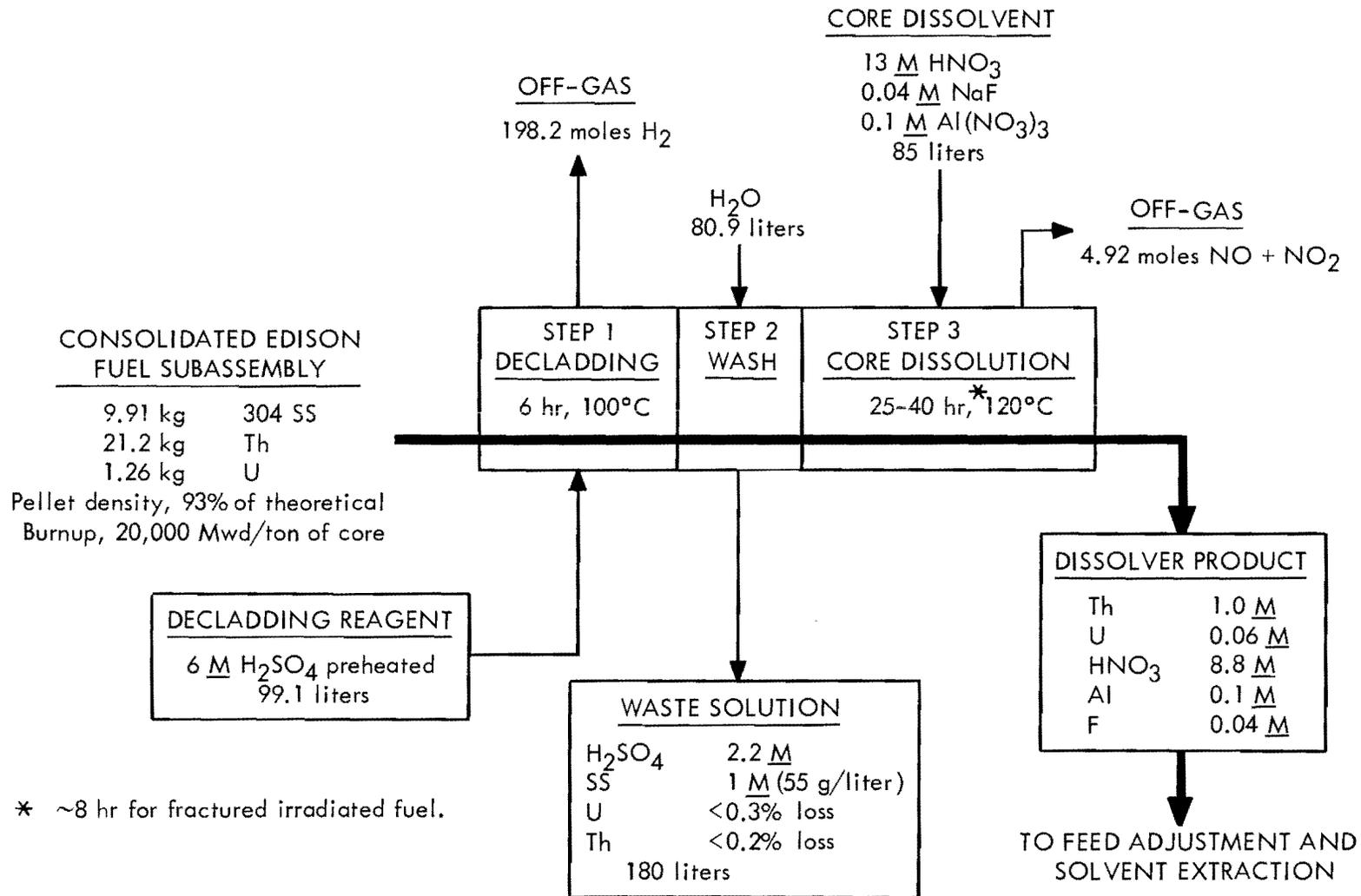


Fig. 15. Decladding and dissolution of Consolidated Edison reactor fuel by the Sulfex-Thorex process.

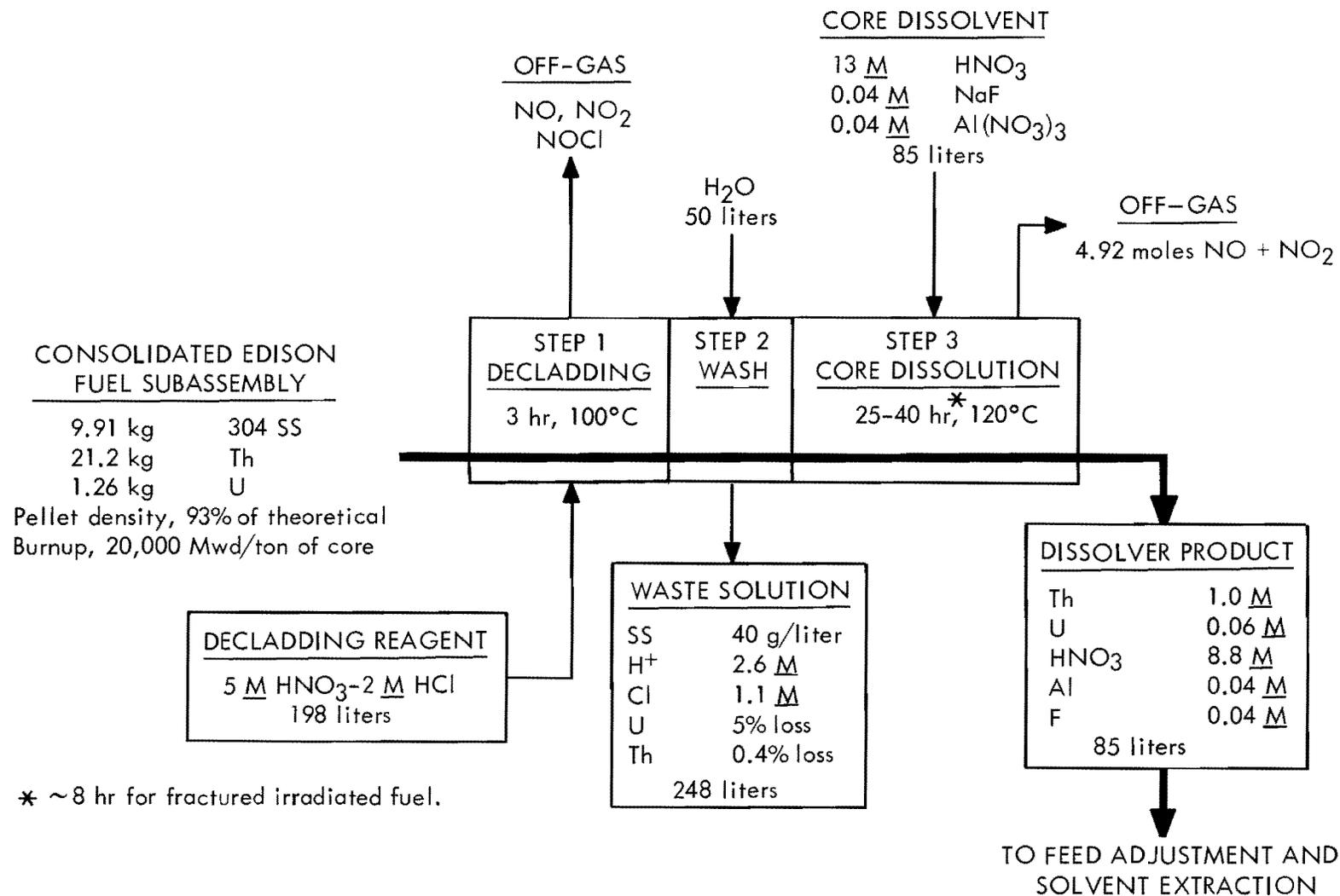


Fig. 16. Decladding and dissolution of Consolidated Edison reactor fuel by the Darex-Thorex process.

containing about 50 grams of stainless steel per liter. The off-gas contains 20% NO<sub>2</sub>, 35% NOCl, 35% nitrogen, and traces of N<sub>2</sub>O, NO, HCl, Cl<sub>2</sub>, and H<sub>2</sub>. 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;<sup>14,23</sup> 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. 4.0).

### 3.1.3 Aluminum Dissolution

Aluminum cladding from ThO<sub>2</sub>-UO<sub>2</sub> fuels such as the BORAX-IV is readily dissolved<sup>28</sup> in NaOH-NaNO<sub>3</sub> solutions with a uranium loss of less than 0.2%. The BORAX-IV fuel, which contained a lead bond between the ThO<sub>2</sub>-UO<sub>2</sub> fuel and the aluminum cladding, was processed at ICPP<sup>29</sup> using the method developed at ORNL.<sup>28</sup> The aluminum cladding was dissolved in caustic and the lead bond dissolved in dilute nitric acid prior to dissolution of the core in 13 M HNO<sub>3</sub>-0.04 M HF.

### 3.1.4 Zirconium Dissolution

Preliminary experiments<sup>17</sup> with unirradiated ThO<sub>2</sub>-UO<sub>2,7</sub> fuel specimens (4.2% UO<sub>2,7</sub>, 83% of theoretical density) indicated that the zirconium cladding could be dissolved in boiling 6 M NH<sub>4</sub>F-1 M NH<sub>4</sub>NO<sub>3</sub> (Zirflex process<sup>25-27</sup>) with attendant uranium and thorium losses of less than 0.4%. Losses would undoubtedly be even lower with higher density UO<sub>2,0</sub> fuel pellets.

### 3.1.5 ThO<sub>2</sub>-UO<sub>2</sub> Core Dissolution

Thorium metal, thorium oxide, and ThO<sub>2</sub>-UO<sub>2</sub> fuel mixtures dissolve in boiling nitric acid containing hydrofluoric acid as catalyst.<sup>17,18,30</sup> Dissolution of high (greater than 90% of theoretical) density fuel pellets in the optimum reagent, 13 M HNO<sub>3</sub>-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-inch-diam CETR fuel pellets.

The rate of dissolution of ThO<sub>2</sub>-UO<sub>2</sub> mixtures containing up to 10% UO<sub>2</sub> depends on the nitric acid concentration, the HF 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 ThO<sub>2</sub>-4.4% UO<sub>2</sub> 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 = reaction rate, mg g<sup>-1</sup> min<sup>-1</sup>; M = nitric acid concentration in the dissolvent, molarity; and M<sub>Th</sub> = thorium concentration in the dissolvent, molarity. The dissolution rate of ThO<sub>2</sub>-5% UO<sub>2</sub> pellets decreases with increasing pellet density; the initial rate in boiling 13 M HNO<sub>3</sub>-0.04 M NaF-0.1 M Al(NO<sub>3</sub>)<sub>3</sub> decreased from 18 to about 1 mg min<sup>-1</sup> cm<sup>-2</sup> as the pellet density increased from 60 to 95% of theoretical. The rates of dissolution of ThO<sub>2</sub> and ThO<sub>2</sub>-UO<sub>2</sub> pellets containing up to 10% UO<sub>2</sub> were essentially the same when the other conditions, such as pellet density, were constant.<sup>24</sup>

Fused  $\text{ThO}_2$ , as expected, dissolved more slowly than material of lower density. For example, in 5-hr experiments with -4+8 mesh samples, only about 30% of the fused  $\text{ThO}_2$  sample dissolved in 200% excess of boiling 13 M  $\text{HNO}_3$ -0.04 M  $\text{NaF}$ -0.1 M  $\text{Al}(\text{NO}_3)_3$  compared to 88% of a sample of 95.8%  $\text{ThO}_2$ - $\text{UO}_{2.36}$  which was 93% of theoretical density.<sup>24</sup> Both unirradiated and irradiated (15,000-20,000 Mwd/T) 8-20 mesh fuel samples were greater than 99% dissolved in a 5-hr reaction with 200% excess of boiling 13 M  $\text{HNO}_3$ -0.01 M  $\text{NaF}$ -0.1 M  $\text{Al}(\text{NO}_3)_3$ . The small residue was dissolved in a second digestion with fresh reagent.<sup>14</sup> Soluble neutron poisons,  $\text{H}_3\text{BO}_3$  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 micron diam  $\text{UC}_2$ - $\text{ThC}_2$  fuel particles coated with 25 to 60 microns 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.<sup>31-34</sup> For elements containing coated fuel particles, however, only two techniques appear applicable. These are burning in oxygen followed by dissolution of the  $\text{ThO}_2$ - $\text{U}_3\text{O}_8$  ash in boiling 13 M  $\text{HNO}_3$ -0.04 M  $\text{F}$ , 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 technique 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  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , or  $\text{HNO}_3$ .<sup>38,39</sup>

### 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<sup>33,34</sup> (Table 3). This technique may also be applicable to fuels containing BeO-coated particles using techniques developed for the dissolution of sintered BeO;<sup>37</sup> however, alumina-coated fuels probably cannot be processed by an aqueous technique because of the chemical inertness of sintered Al<sub>2</sub>O<sub>3</sub>. The Al<sub>2</sub>O<sub>3</sub>-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 <sub>2</sub> -ThC <sub>2</sub>	1.7	8.0	13 M HNO <sub>3</sub> -0.04 M HF 0.1 M Al(NO <sub>3</sub> ) <sub>3</sub>	100	100
Pyrolytic carbon-coated UC <sub>2</sub> -ThC <sub>2</sub>	9.9	33.0	13 M HNO <sub>3</sub> -0.04 M HF- 0.1 M Al(NO <sub>3</sub> ) <sub>3</sub>	100	100
Al <sub>2</sub> O <sub>3</sub> -coated UO <sub>2</sub>	8.0	0.0	10 M HNO <sub>3</sub>	9.9	---

### 3.2.2 Fine Grinding Followed by Acid Leaching

After a fuel containing carbon-, BeO-, or Al<sub>2</sub>O<sub>3</sub>-coated fuel particles is ground fine enough to ensure rupture of the particles (about 200 mesh), the uranium and thorium can be recovered<sup>33,34</sup> by leaching with either nitric acid or HNO<sub>3</sub>-HF (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 <sub>2</sub> O <sub>3</sub> -coated UO <sub>2</sub>	8.0	0.0	15.8 <u>M</u> HNO <sub>3</sub>	99	---
Pyrolytic carbon-coated UC <sub>2</sub> -ThC <sub>2</sub>	9.7	33.8	15.8 <u>M</u> HNO <sub>3</sub>	~99	99.9
Pyrolytic carbon-coated UC <sub>2</sub> -ThC <sub>2</sub>	9.6	33.5	13 <u>M</u> HNO <sub>3</sub> - 0.04 <u>M</u> HF- 0.1 <u>M</u> Al(NO <sub>3</sub> ) <sub>3</sub>	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.<sup>35,36</sup> 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<sub>2</sub>C<sub>3</sub>, ThC<sub>2</sub>, UC<sub>2</sub>, results in much less gas evolution. However, the gas contains 30-40% C<sub>2</sub>-C<sub>8</sub> hydrocarbons and 50-80% hydrogen. Furthermore, 50-80% of the carbide carbon remains as non-volatile carbon compounds. Hydrolysis of the respective carbides yields about the same gaseous products in 6 N HCl and 6 M H<sub>2</sub>SO<sub>4</sub> as in water. On the other hand, reaction of UC with 4 M HNO<sub>3</sub> gives completely

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

	Carbide				
	UC	ThC	U <sub>2</sub> C <sub>3</sub>	UC <sub>2</sub>	ThC <sub>2</sub>
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 <sub>2</sub> -C <sub>8</sub> 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

different results. The off-gas is comprised mainly of NO and CO<sub>2</sub> and contains no hydrogen or hydrocarbon gases (Table 6). In addition, 30-50% of the carbide carbon

Table 6  
Reaction of UC with 4 M HNO<sub>3</sub>

Product	% of Total Carbon in Product	Product Composition
Off-gas	50-70	77% NO; 19% CO <sub>2</sub> ; 4% N <sub>2</sub> 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.

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<sub>2</sub>. These carbides hydrolyze completely in a few hours at 80°C whereas about 24 hr are required for U<sub>2</sub>C<sub>3</sub> and UC<sub>2</sub> at the same temperature (Fig. 17). Specific reaction rates cannot be obtained because samples (3-4 grams each) disintegrate to powder within ~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.<sup>35</sup>

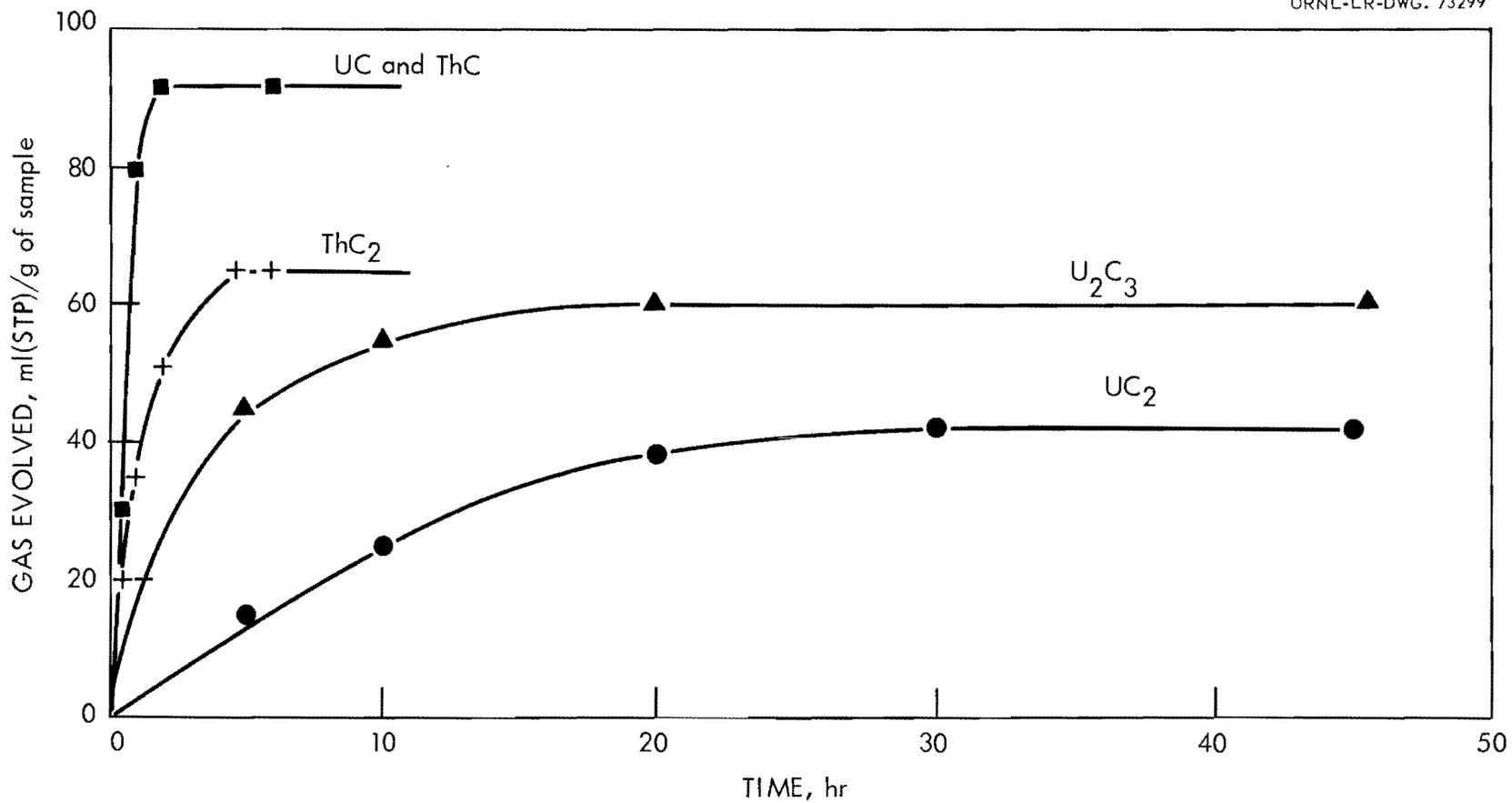


Fig. 17. Relative rates of hydrolysis at 80°C of 3 to 4 g samples of uranium and thorium carbides in water.

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 chopping followed by steaming or reaction with liquid water to destroy the bond and hydrolyze the carbon 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 organic materials. 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<sub>3</sub> reaction; in this case, there should be no problem presented to further processing.

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 HNO<sub>3</sub>. 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-HNO<sub>3</sub> reaction, the products were not nitrated and should not constitute a process hazard.

#### 4.0 SOLVENT EXTRACTION

"Acid" solvent extraction processes have been developed for the extraction of uranium-233 (Acid Interim 23 process)<sup>38</sup> or co-extraction of uranium and thorium (Acid Thorex process)<sup>39</sup> 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 differ from previous flowsheets<sup>40</sup> 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 techniques. 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.<sup>41</sup>

#### 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).  $\text{Pa}^{233}$ , 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 not effective as a salting agent. The volume of the evaporated waste is 1/10 that from the Interim 23 process. Decontamination factors obtained were 1000, 5000, 1000, and  $10^5$ , 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 acidic feed was used, decontamination was reduced by a factor  $> 10$ .<sup>42</sup> 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 acidic sections of the column. In laboratory countercurrent experiments, the fission products contacted the aqueous media for approximately 20 minutes. In pulse columns this time would be reduced to

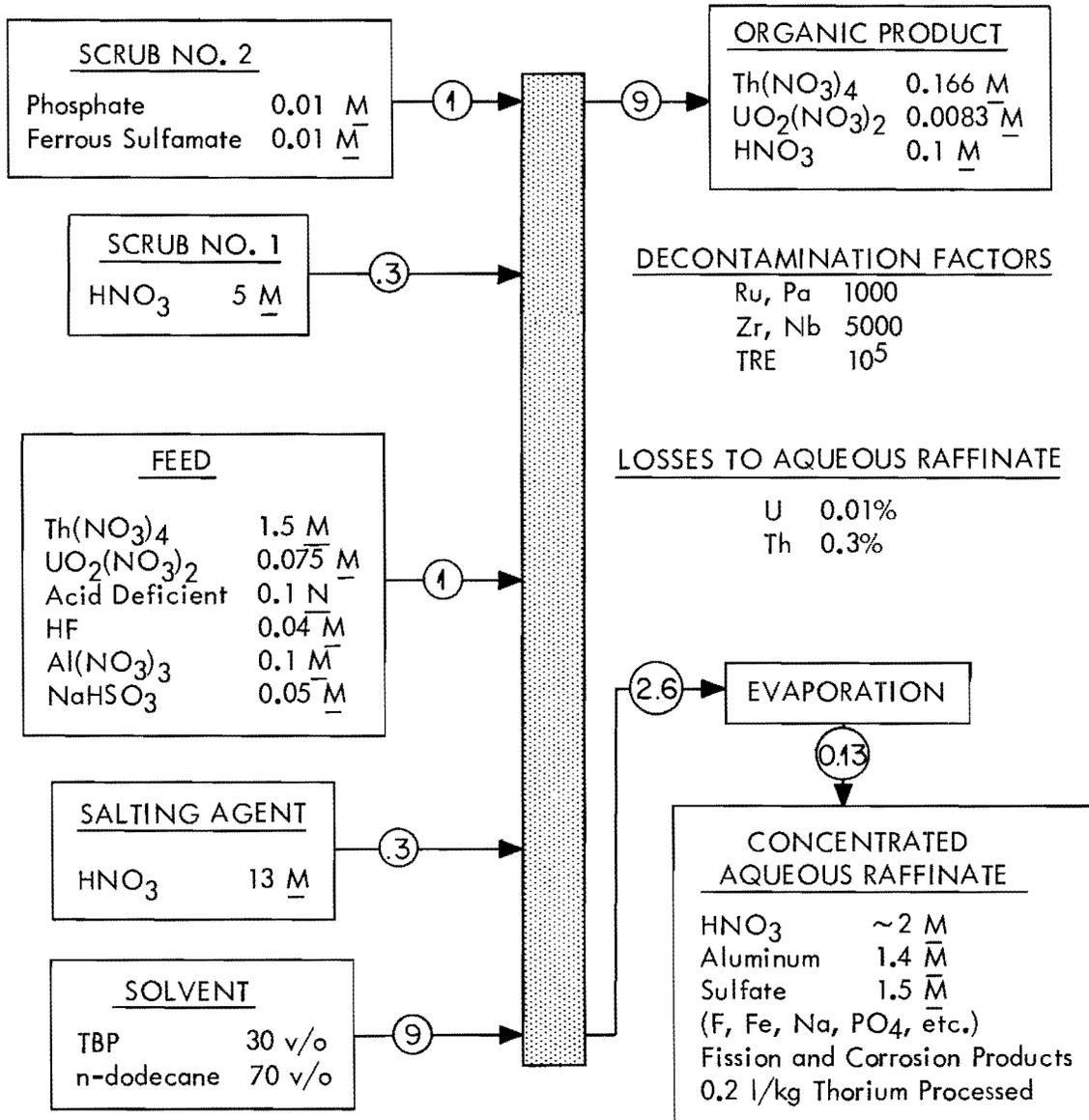


Fig. 18. Acid Thorex process.

about 8 minutes. The two scrub solutions shown in the flowsheet combine to form a 1 M HNO<sub>3</sub> 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 separate partitioning and strip columns, a single 1 M HNO<sub>3</sub>, 0.01 M PO<sub>4</sub><sup>=</sup>, 0.01 M FeHSO<sub>3</sub> scrub solution at a relative flow rate of 1.3 is satisfactory.

#### 4.2 Acid Interim 23 Process

An Acid Interim 23 process was developed<sup>38</sup> to extract uranium-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 protactinium-233 has decayed to uranium-233, the wastes can be re-extracted using 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 non-critically safe equipment, 2.5% TBP is used to limit the U-233 concentration in the organic phase. Uranium loss was <0.01% and the gross decontamination factor was ~10<sup>5</sup>. 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 2nd time to recover Pa-233 and the relatively large waste volume.

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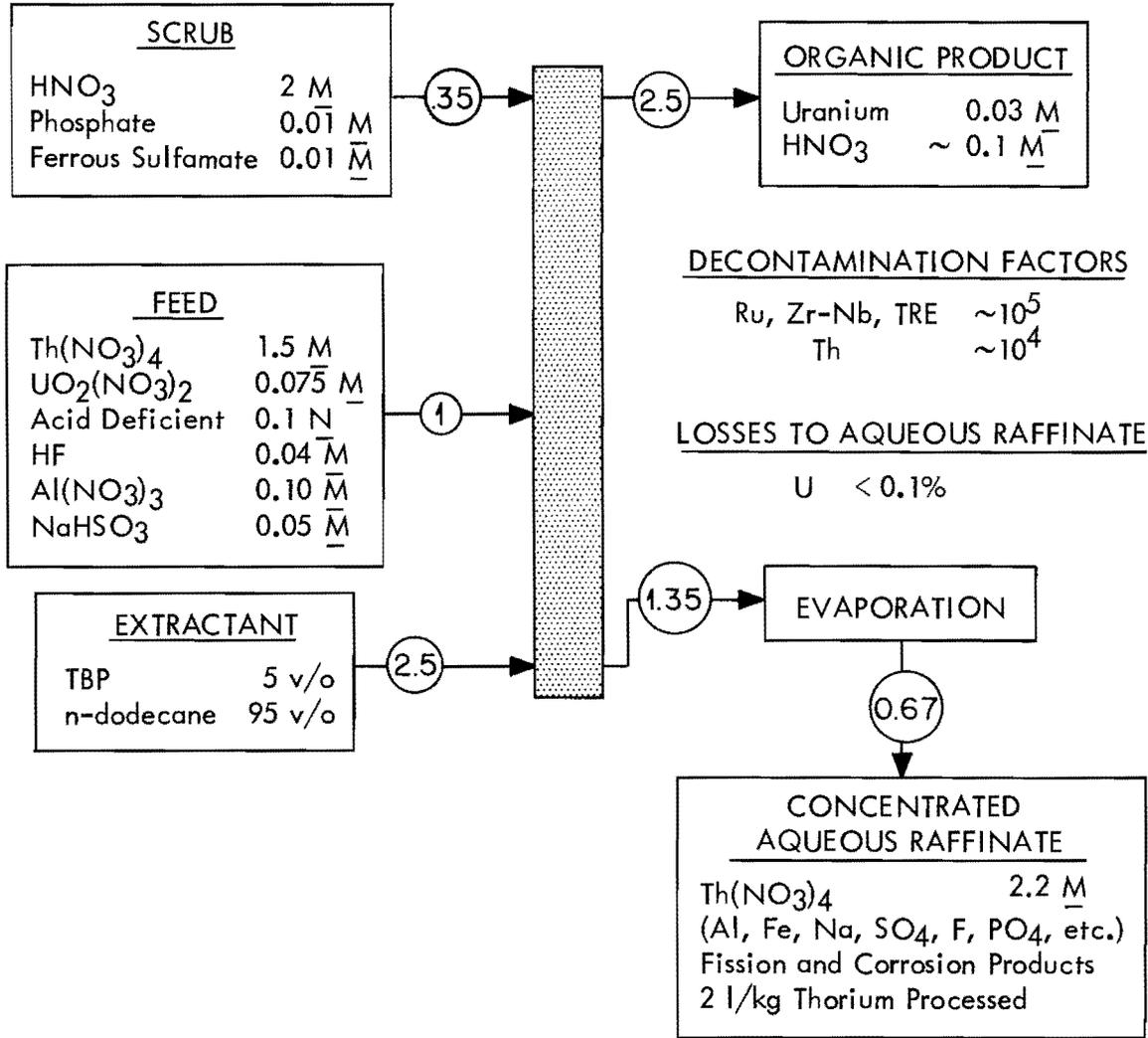


Fig. 19. Acid Interim-23 process.

### 4.3 Kilorod Program

A solvent extraction flowsheet was developed<sup>43</sup> for purifying recovered U-233 to be used in the fabrication of fuel elements by the Sol-Gel process<sup>44</sup> (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 higher by a factor of four in the DSBPP system at thorium concentrations less than 100 g/l.<sup>45,46,47</sup> 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. Decontamination from Th-228 and its' daughters is  $\sim 10^4$ . Since DSBPP is not soluble in dodecane, an aromatic diluent, di-ethyl benzene 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 hours 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 semi-remote Sol-Gel, vibratory-compaction equipment for at least 10 days without over exposure to operating personnel. 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.<sup>48</sup>

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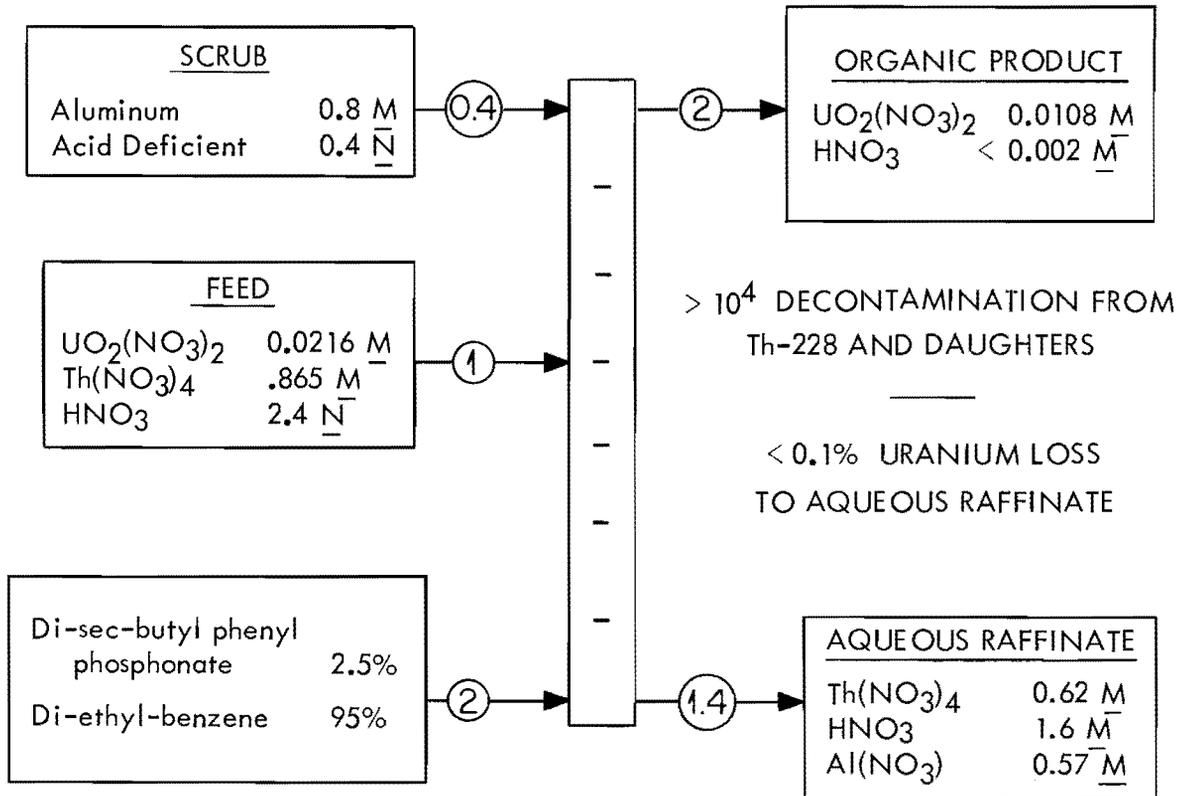


Fig. 20. Kilorod Interim-23 process.

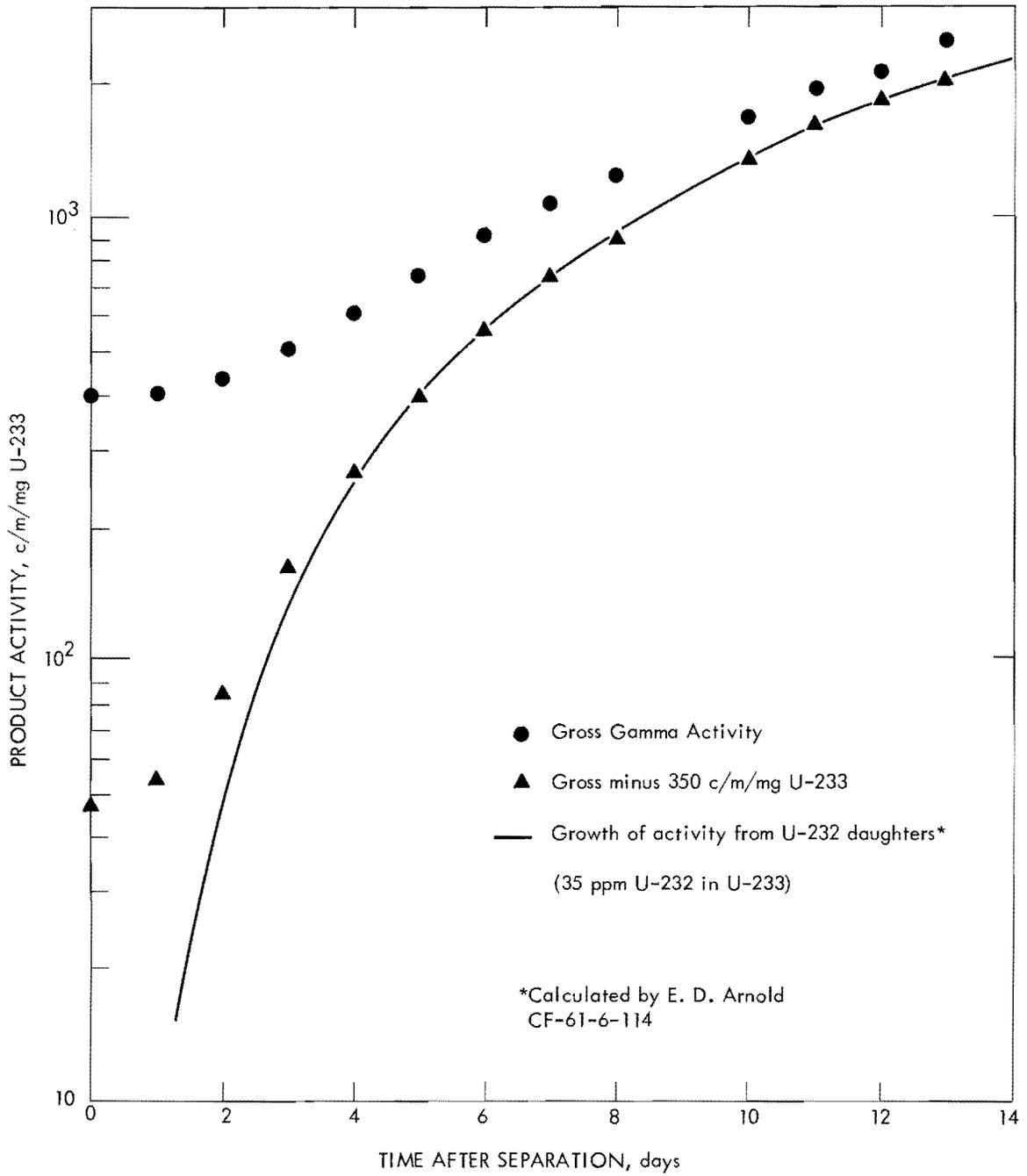


Fig. 21. Growth of activity in U-233 following solvent extraction purification.

#### 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 Int-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 adsorption of protactinium from highly acidic dissolver solution on silica gel or unfired powdered Vycor glass or the coextraction of the protactinium with the thorium and uranium using a Thorex type solvent extraction flowsheet.

Solubility studies using Pa-231 have shown that protactinium remained homogeneously dispersed in solutions equivalent to those to be obtained in dissolution and feed of Consolidated Edison fuel irradiated to 20,000 Mwd/ton. The solutions contained 116 g/l Th, ~0.07 g/l Pa, 11 M HNO<sub>3</sub>, 0.1 M Al and <0.1 M F and 40 g/l Th, 0.09 g/l Pa, 5 M HNO<sub>3</sub>, 1 M Al, and ~0.1 M F and showed no decrease in protactinium concentration after standing in a plastic container one month at room temperature. These solutions also showed no change in concentration after contacting either welded or unwelded 347 stainless steel coupons for 1 week at room temperature.<sup>49</sup> These solubilities are in agreement with the observations of Hardy et al.<sup>50</sup> that protactinium stock solutions containing 10<sup>-3</sup> M Pa in 6 N HNO<sub>3</sub> were stable for many months.

Laboratory experiments demonstrated that at least 90% of the protactinium in the synthetic dissolver solution could be adsorbed on columns containing either unfired Vycor glass or laboratory prepared silica gel.<sup>51</sup> When the experiments were terminated, the columns contained 1.6 and 3.2 mg Pa per gram adsorbent, respectively. The amount of protactinium not absorbed remained constant throughout the experiment. The protactinium was eluted at six times the feed concentration with 0.5 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. This greatly decreases the activity which must be handled in later processing equipment.

A low decontamination "Acid Co-Extraction Process" is also being developed<sup>52</sup> for the recovery of protactinium in which protactinium, uranium, and thorium are simultaneously extracted from highly acidic feed solutions with 30% TBP. In experiments with tracer protactinium, about 90% of the protactinium was extracted from 5 M HNO<sub>3</sub>, 1 M Al(NO<sub>3</sub>)<sub>3</sub> resulting in a decontamination factor of 70 from ruthenium and ~10<sup>5</sup> from rare earth elements. 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 essentially free of U-232 which is valuable for special uses.

## 5.0 CHOICE OF PROCESSING METHOD

The choice of processing method depends on which of the following objectives must be met (1) short cooling times with immediate co-recovery of uranium-233, thorium, and protactinium vs long cooling for complete decay of protactinium-233 to uranium-233 before recovery of uranium-233 and thorium; or (2) short cooling time and recovery of uranium-233 alone in a first cycle followed by recovery of additional uranium-233 (and thorium, if desired) after complete decay of protactinium-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. The radiation and processing problem presented by these alternatives to subsequent fuel processing steps are outlined in other papers.<sup>53,54</sup>

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 protactinium-233 recovery from nitrate solution has been done on a tracer scale. Experiments with macro amounts of protactinium-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<sup>50</sup> (see Sec. 4.4). Thus the Acid Thorex process could be used for direct recovery of uranium-233 and thorium in short cooled processing after protactinium adsorption or after complete decay of protactinium-233 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<sup>52</sup> can probably be used to recover uranium, thorium, and protactinium simultaneously. The low decontamination factors for zirconium and niobium may not be significant since Zr-Nb have low cross-sections and remote fuel fabrication is required in any event.

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 U-233 processing rate is 2-3 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 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. As 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 with 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 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 only be increased by 20% if recycled thorium is used.<sup>44</sup> 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.

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