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ABSTRACT

Increasing emphasis has been placed recently on the application of solvent extraction to the recovery of uranium and plutonium from spent power reactor fuels. Zircaloy-2 jackets were removed from PWR blanket-type fuels by dissolution with the Zirflex process, and the UO_2 cores were dissolved in 10 M HNO_3. Zirflex treatment of prototype samples irradiated to 2500 Mwd/ton resulted in satisfactory dissolution rates and losses to the dejacketing solution generally less than 0.2% for uranium and plutonium. Zirconium-uranium alloy fuels were dissolved in 6 M NH_4F and adjusted for solvent extraction by the addition of $Al(NO_3)_3$ and HNO_3. In an alternative procedure, fluoride was recycled by metathesis and precipitation. Stainless steel jackets were removed from Consolidated Edison-type fuels by dissolution in 6 M H_2SO_4 (Sulfex process), and the ThO_2-UO_2 core was dissolved in 13 M HNO_3-0.04 M F-0.04 M Al. Dejacketing losses in unirradiated samples were about 0.02%. Use of the ORNL Reference Darex flowsheet for APPR processing resulted in solvent extraction feed containing 30 ppm chloride. Mechanical equipment was designed to declad SRE fuel, and chop and leach techniques are being developed to treat stainless and zirconium clad ceramic fuel.

A solvent extraction flowsheet was developed for Foreign Research Reactor Fuels, (Al-20% enriched U alloy) using a revised tributyl phosphate extraction system for the separation of plutonium from uranium. Feasibility tests were carried out on the coupling of Redox solvent extraction with Darex and Niflex head-end treatments. New solvents for the reprocessing of power reactor fuels are being studied. Among these, the amines show an order of magnitude greater radiation stability than does tributyl phosphate. A primary amine was proposed for the recovery of uranium and plutonium from Sulfex decladding wastes.

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INTRODUCTION

Solvent extraction remains as a proven versatile reprocessing method and will be used for reprocessing power reactor fuels in the immediate future. New head end techniques are required, however, to adapt zirconium, niobium and stainless steel bearing alloy and ceramic fuels to the solvent extraction processes. Both chemical and mechanical head end methods are being considered. In many cases new variations in solvent extraction processes are required to compensate for projected increases in radiation level, fission product concentrations, and macro impurity concentrations. This paper reviews developments which have occurred since the Second Geneva Conference on Peaceful Uses of Atomic Energy in September 1958. Papers (1,2,3) reported at the Geneva Conference covered data obtained up to that time. The resumes given are intentionally brief. Details can be obtained in the references cited.

FEED PREPARATION

Zirconium Bearing Fuels

Zircaloy Jacket Dissolution in Ammonium Fluoride (Zirflex Process). Dissolution in aqueous ammonium fluoride is being studied as a method for removing zirconium bearing jackets from fuels with oxide cores. The PWR blanket is a typical example of this fuel type. The flowsheet shown in Fig. 1 supercedes those reported previously.(1,4) Pertinent dissolution rate and solubility data were also reported in these references. Recent development work has adapted the flowsheet to allow incomplete end cap dissolution and the removal of fluoride from UO_2 pellets prior to their dissolution in nitric acid. The end caps will accumulate and will be dissolved in special cleanup cycles.

The Zircaloy-2 jacket is dissolved with boiling 6 $\underline{M}$ NH_4F-1.0 $\underline{M}$ NH_4NO_3 solution. The ammonium nitrate accomplishes the dissolution of the tin

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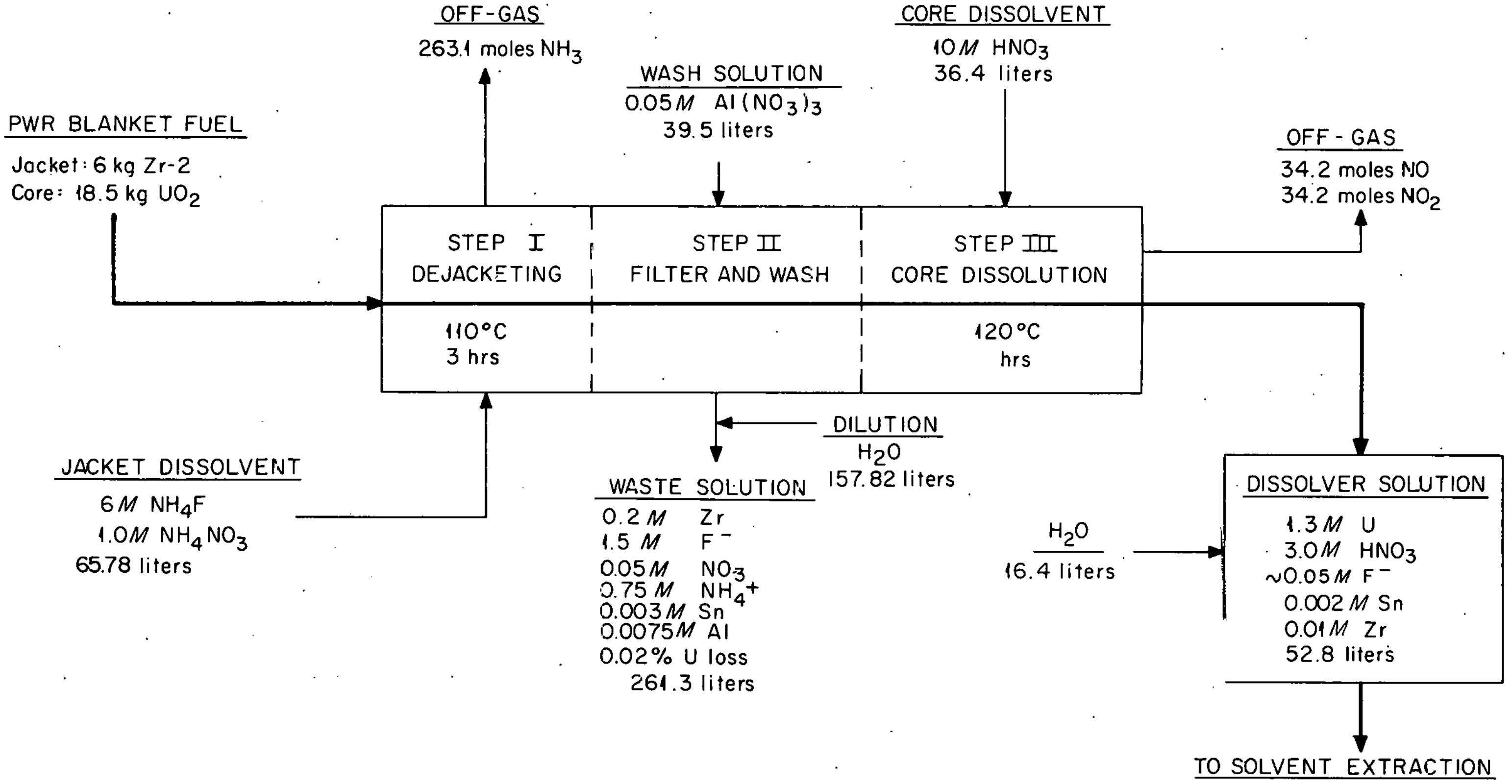

Fig. 1. Zirflex Process for Dejacketing Zircaloy Jacketed Fuel With Ammonium Fluoride.

contained in Zircaloy and prevents the evolution of hydrogen. About 6 moles of fluoride are used per mole of zirconium in the fuel to maintain high dissolution rates. The solid end caps, which constitute about 20 wt % of the total zirconium, are not dissolved in the time required for decladding so that the actual F/Zr mole ratio in solution can be as high as 10. Consequently, the decladding waste solution is diluted fourfold to avoid precipitation of $(NH_4)_3ZrF_7$. The solubility at 25°C of $(NH_4)_3ZrF_7$ is about 1 molar in water but decreases with increasing NH_4F concentration to about 0.2 molar at a F/Zr mole ratio of 10.

After decladding, the UO_2 fuel pellets are washed with 0.05 M $Al(NO_3)_3$ solution to remove adhering fluoride prior to their dissolution in nitric acid. With this treatment, the fluoride concentration in the solvent extraction feed solution is about 0.05 M compared to 0.1 to 0.2 M if water is used as the wash. The $Al(NO_3)_3$ solution is used to partially dilute the decladding waste solution.

The UO_2 core pellets are readily dissolved in 10 M HNO_3 and the product solution can be diluted to yield a satisfactory solvent extraction feed solution containing 1.3 M $UO_2(NO_3)_2$ and 3 M HNO_3.

Austenitic stainless steel appears to be a suitable material of construction for the Zirflex process. A corrosion rate of 30 mils/yr has been reported for cyclic tests simulating Zircaloy-2 jacket removal with boiling 6 M NH_4F-0.5 M NH_4NO_3 and UO_2 dissolution in 10 M HNO_3.(1)

Effect of Fuel Irradiation on the Zirflex Process. Irradiated PWR-blanket fuel specimens were dejacketed by two methods, i.e., dissolution of the Zircaloy-2 jacket in 6 M NH_4F-1.0 M NH_4NO_3 or in 9 M HF.(5) In both cases the UO_2 core was dissolved in 10 M HNO_3. The experiments were conducted in a Carpenter-20 vessel. Irradiation conditions for the fuel samples varied from 250 to 2500 Mwd/T of uranium at 110 to 600°F and water pressures up to 2200 psig (Table 1). Neither irradiation conditions nor length of contact time between the core and decladding solution produced any noticeable variation in dissolution rates or losses of uranium or plutonium to the dejacketing solution or to a nitric acid insoluble precipitate. Decladding periods as short as 3 hr provided complete

Table 1. Uranium and Plutonium Losses in the Zirflex Process Using Irradiated Fuel Samples

Conditions

PWR Blanket Pin - 0.050 kg Zr-2, 0.133 kg UO_2
Jacket Dissolvent - 6 $\underline{M}$ NH_4F-1.0 $\underline{M}$ NH_4NO_3, 0.5 L, or 9 $\underline{M}$ HF 0.6 L, boiling
Water Wash - 0.3 L
Core Dissolvent - 10 $\underline{M}$ HNO_3, 0.3 L, boiling

Run No.	Decladding Reagent	Decladding Period (hr)	Loss to Decladding Solution (%) U, %	Loss to Decladding Solution (%) Pu, %	Loss to HNO_3 Insoluble Precipitate (%) U	Loss to HNO_3 Insoluble Precipitate (%) Pu	Irradiation Data: Approximate Burnup, Mwd/T	Irradiation Data: T, °F	Irradiation Data: Water Pressure, Psig
1	6 $\underline{M}$ NH_4F^--1 $\underline{M}$ NH_4NO_3	5	0.032	0.008	0.01	0	250	110	12
2		6	0.17	0.23	0	0	250	110	12
3		7	0.53	0.090	0	0.18	250	110	12
4		6	0.13	0.021	0.66	2.23	500	500-600	1800-2200
5		6	0.25	0.039	0.01	0.02	500	500-600	1800-2200
6		6	0.074	0.059	0.41	0.53	500	500-600	1800-2200
7		10	0.099	0.084	0.75	1.53	500	500-600	1800-2200
8		3	0.13	0.15	0.37	0.51	500	500-600	1800-2200
9		9	0.092	0.050	*	*	500	500-600	1800-2200
10	9 $\underline{M}$ HF	3	1.270	0.510	*	*	500	500-600	1800-2200
11		3	0.83	0.260	*	*	500	500-600	1800-2200
12	6 $\underline{M}$ NH_4F^- 1 $\underline{M}$ NH_4NO_3	5	0.042	0.013	*	*	2500	115	9-48
13		10	0.110	0.060	*	*	2500	115	9-48
14		10	0.088	0.058	*	*	2500	115	9-48
15		5	0.23	0.48	*	*	1000	500-600	1800-2200
16		10	0.17	0.30	*	*	1000	500-600	1800-2200
17		7	0.20	0.15	0.01	0.04	1900	500-600	1800-2200

*No precipitate formed.

removal of the jacket. The uranium and plutonium losses to the 6 M NH_4F-1.0 M NH_4NO_3 solutions, while higher than found with unirradiated pins, were acceptable, i.e., less than 0.2% in nearly all cases. The uranium and plutonium losses to the 9 M HF solutions averaged 1.0 and 0.4%, respectively, corresponding to loss levels obtained with unirradiated specimens.(6)

After the decladding step, the UO_2 pellets were dissolved in 10 M HNO_3. In some cases when NH_4F-NH_3NO_3 was used as the decladding agent, a nitric acid insoluble residue remained after core dissolution. This unidentified precipitate contained up to 0.8% of the uranium, 2.3% of the plutonium, an average of 23% of the zirconium and a large amount of fluoride. Significantly, there were many cases, including the most highly irradiated samples, where no precipitate was formed when NH_4F-NH_4NO_3 was used and a precipitate was not formed when HF was used. The nitric acid insoluble precipitate appears to be related to contamination of the core solution with $(NH_4)_3ZrF_7$ which could have precipitated from the decladding solution. The revised flowsheet (Fig. 1) is designed to prevent the precipitation of $(NH_4)_3ZrF_7$. Consequently, loss of uranium and plutonium to an insoluble precipitate is not expected. Further tests on irradiated samples are being made.

Zirconium-Uranium Fuel Alloy Dissolution in Ammonium Fluoride (Modified Zirflex Process). New processes have been developed for dissolving zirconium- and niobium-bearing alloy fuels using unirradiated fuel samples.(7) Dissolution problems with this fuel type stem from the impractically low rate of dissolution of zirconium in nitric acid, the explosive reactions of U-Zr or U-Nb alloys with nitric acid in the absence of fluoride, and the corrosive action of mixtures of hydrofluoric and nitric acid on materials of construction. For example, in the present process for dissolution of Zircaloy-2 clad STR fuel (97% Zr-1% U-2% Sn),(8) a Monel tank is used to dissolve the Zircaloy-2 jacket in hydrofluoric acid and a stainless steel tank, for feed adjustment and oxidation of U(IV) to U(VI). Fuels containing more than 1% uranium are not easily processed because of the low solubility of UF_4.

The new process proposes dissolution in NH_4F followed by the addition of nitric acid and $Al(NO_3)_3$ to form a solution of approximately the same composition as the present STR process, with the exception that the uranium concentration can be higher and that it also contains 2.3 M NH_4^+ (ammonium ion), (Fig. 2). Consequently, the present STR solvent extraction process can be used with the new dissolution treatment. Advantages of this process are the rapid dissolution rate of Zr and Nb alloys and the low corrosion rate of stainless steel in ammonium fluoride solutions. Hence a single stainless steel dissolver could be used. In addition the process can easily handle fuels, such as the PWR seed, which contain more than 1% uranium. A disadvantage is the precipitation of NH_4UF_5 during the NH_4F dissolution step. The precipitate is readily dissolved when the aluminum nitrate and nitric acid are added, however.

In an alternate flowsheet, the recycle of fluoride in the head end equipment is proposed (Fig. 3). In this case, 14.9 M NH_4OH is added to the ammonium fluoride dissolver solution to precipitate hydrous zirconium oxide and metathesize the solid NH_4UF_5 to hydrous uranium oxide. The oxides are recovered by filtration and washed twice with ammonium hydroxide to increase the amount of fluoride removed. The fluoride-bearing ammonium hydroxide solutions containing about 65% of the fluoride, are heated to remove excess water and ammonia and the residual NH_4F solution recycled to dissolve the next batch of fuel. About 85% of the fluoride can be recycled if additional washes are performed. The uranium and zirconium oxides dissolve readily in nitric acid to form a nitric acid solution suitable for solvent extraction. Aluminum nitrate addition is probably not required to control corrosion by fluoride in the final solution since the removal of fluoride has reduced the ratio of F/Zr to 2.3 or less. The deletion of aluminum from the extraction feed should permit the use of a more concentrated solution thus increasing the throughput rate and decreasing the volume of radioactive waste. Further work is required to define the exact conditions required for solvent extraction.

Two alternative flowsheets developed for the EBWR-Core 1 fuel, 93.5% U-5% Zr-1.5% Nb clad in Zircaloy-2, are similar to those shown in Figs. 2 and 3. In this case, however, it is possible to recycle 97% of the fluoride. A third alternative under study for the EBWR employs

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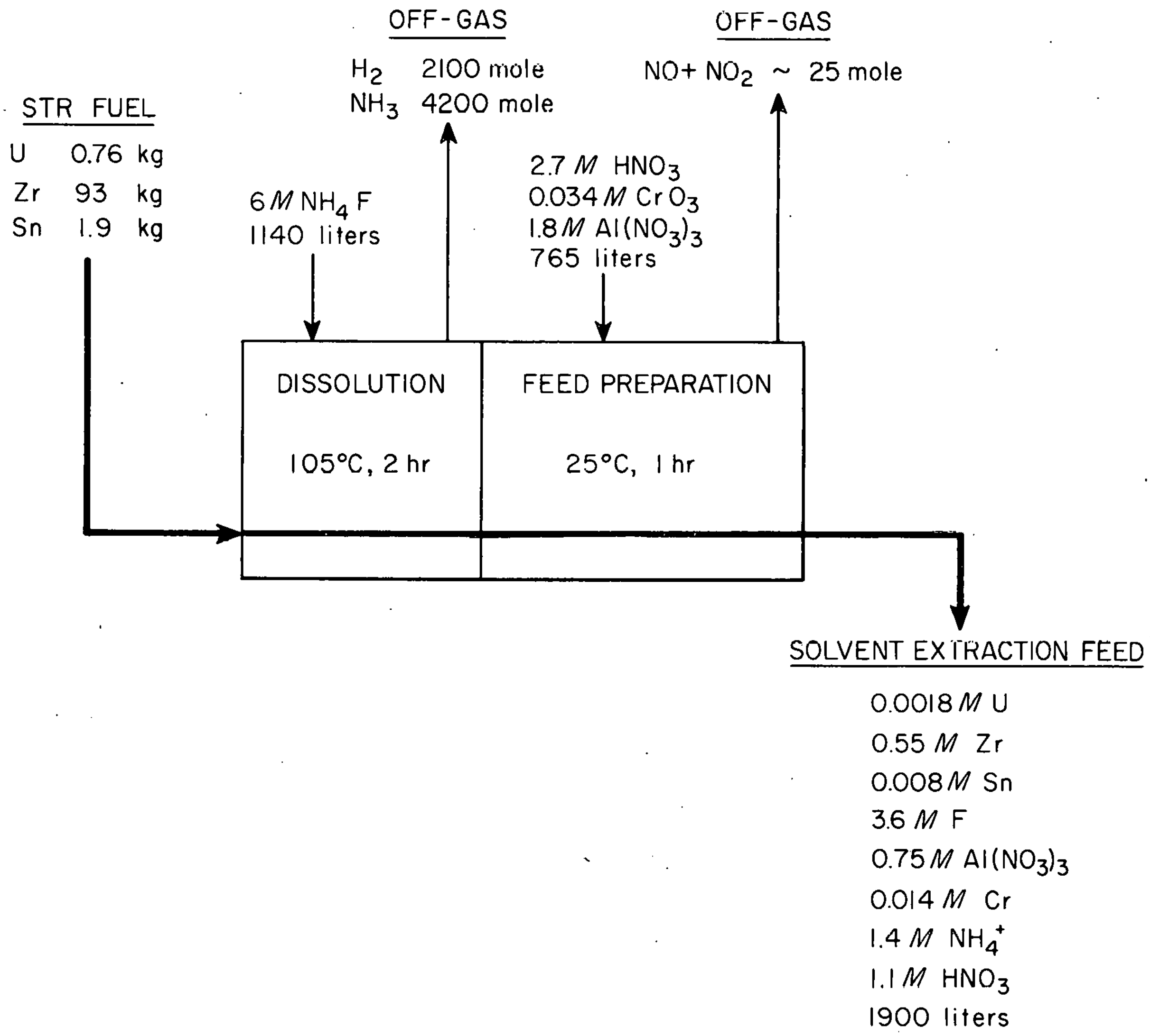

Fig. 2. Modified Zirflex Process for Dissolution of Zirconium-Uranium Alloy Fuel in Ammonium Fluoride.

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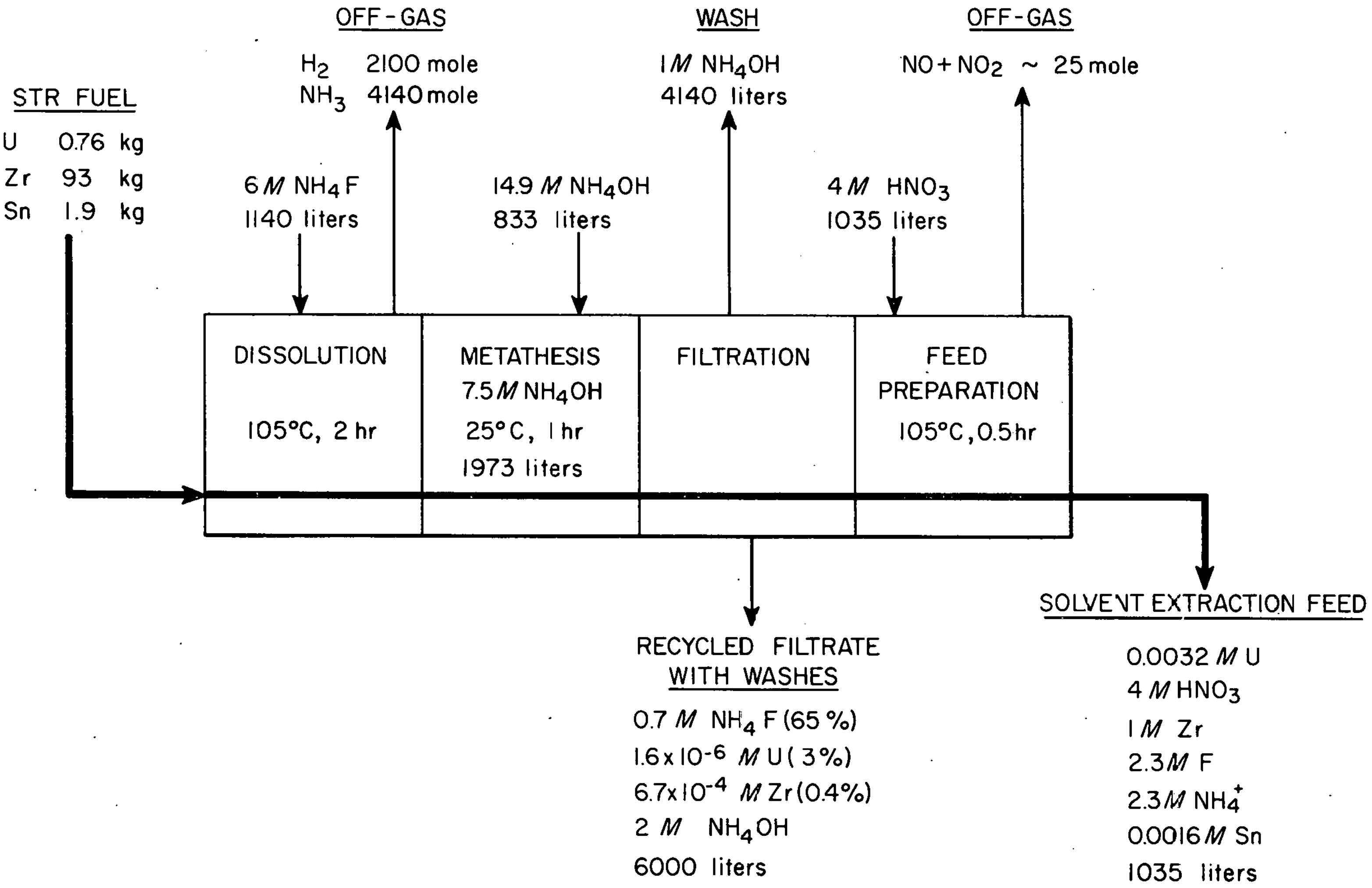

Fig. 3. Modified Zirflex Process for Dissolution of Zirconium-Uranium Alloy Fuel in Ammonium Fluoride with Recycle of Fluoride.

dissolution of the Zircaloy-2 jacket in ammonium fluoride followed by addition of aluminum nitrate and nitric acid to the dejacketing solution to accomplish dissolution of the core. This procedure requires about 80% less fluoride than the case where complete dissolution is accomplished with ammonium fluoride.

Stainless Steel Bearing Fuels

Batch Darex Flowsheets - Several batch flowsheets have been developed for the treatment of stainless steel fuel elements by dilute aqua regia(9)(10). Examples will be given of four batch flowsheets used for the preparation of solvent extraction feed from APPR fuel elements. The basic concept of all three flowsheets is that nitric acid is added to the dissolution product and a mixed nitric-hydrochloric acid stream is removed by batch distillation. More nitric acid is then added to decompose the remaining chloride, and the solvent extraction feed is prepared by distillation and dilution with water.

A very convenient batch flowsheet is afforded through the use of 95 wt % nitric acid (see Figure 4). The product from dissolution may be treated with 95% acid, and a strong acid may be distilled and collected in a make-up tank for preparation of aqua regia for the next dissolution run. More 95% acid is then added and the acidified concentrate is refluxed for two hours. At the end of the reflux period, dilution results in a solvent extraction feed containing less than 350 ppm chloride (the maximum safe concentration of chloride in feed to a stainless steel solvent extraction system).

The advantage of the use of 95% nitric acid is that no waste acid stream must be produced in order to remove water in the system. The main disadvantage is that titanium (the material of construction for all parts of the Darex head-end system) may react explosively with 99% nitric acid, and operating errors or unwanted rectification might produce acid of that strength in the system.

If 61% rather than 95% nitric acid is used for the feed to a Darex head-end treatment, water must be removed at some step in the process. Without rectification equipment, the water is necessarily accompanied by small amounts of nitric and hydrochloric acid, even if the distillate is collected from the most dilute acid solution in the process. All 61% ORNL flowsheets contain a step immediately following dissolution in which a dilute mixed acid stream is removed by distillation. After the dilute acid removal there are two basic methods of treatment with 61% acid to recover a mixed acid and to prepare a low chloride solvent extraction feed.

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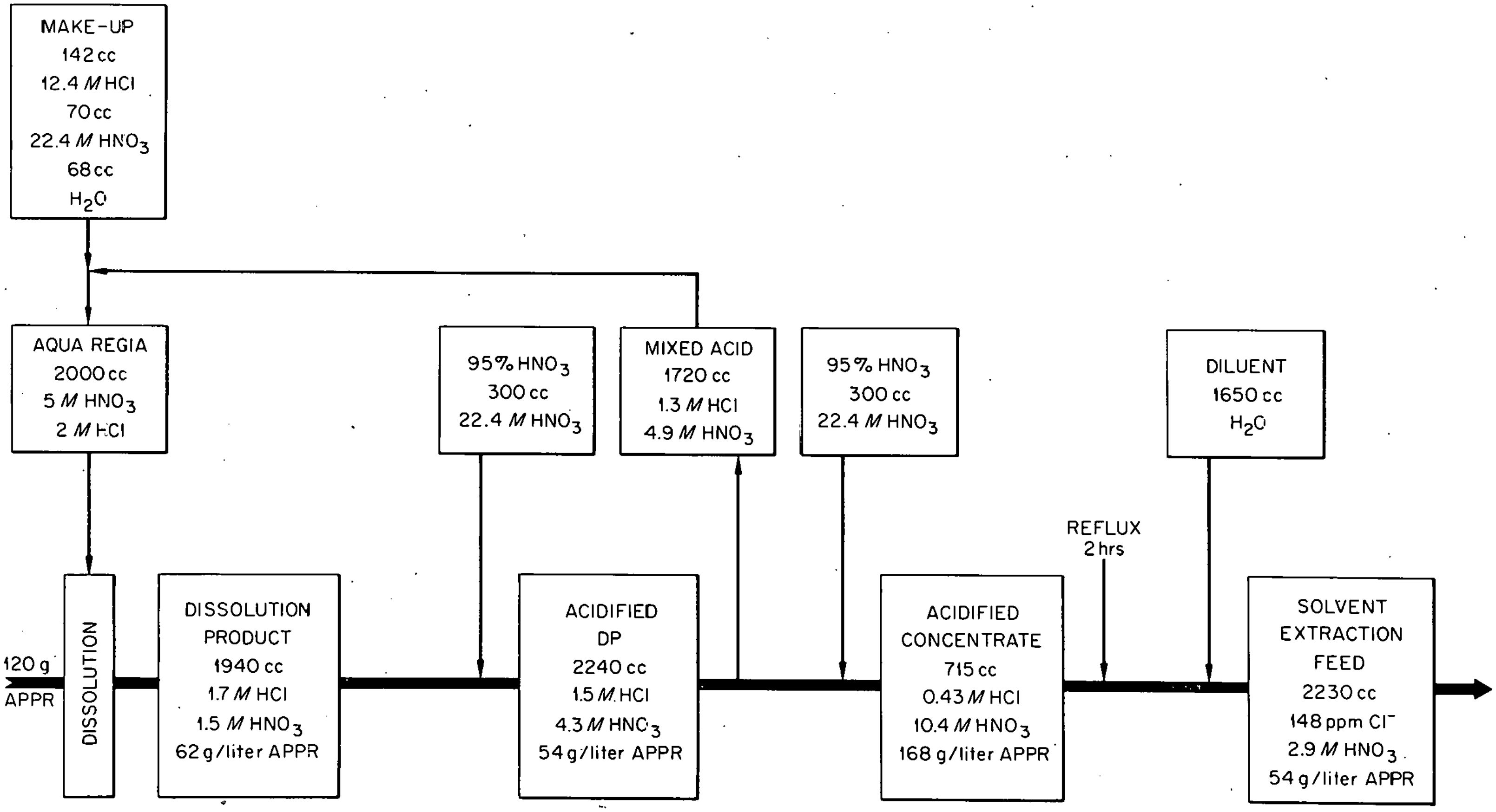

Fig. 4. The Darex Process: Reflux Flowsheet for Batchwise Operation Using 95 wt % HNO_3. Run No. APPR-14.

The two basic methods may be termed the Reflux flowsheet and the Recycle flowsheet. In a Reflux flowsheet 61% nitric acid is added batchwise, and the mixture is refluxed with or without gas sparging to remove low solubility chloride species from the system. After the reflux step, a mixture of nitric and a trace of hydrochloric acid is removed by a single stage batch distillation, producing a concentrated salt solution. In a Recycle flowsheet a strong acid stream is added continuously to a tank from which a mixed acid stream is distilled continuously.

In Figure 5 is shown a 61% Reflux flowsheet similar to that using 95%. The first step after the production of the dissolution product is the removal of a waste stream which is approximately 0.5 molar in nitric and hydrochloric acid. Fresh 61% acid is then added in a single batch and the acidified dissolution product is treated by batch distillation to produce mixed acid for recycle. A second batch addition of 61% acid is made followed by several hours of refluxing with gas sparging, and a batch distillation is carried out to produce slightly dilute nitric acid containing a trace of chloride. This stream can also be returned for reuse. Finally, dilution produces solvent extraction feed meeting the requirements for chloride content.

A Recycle flowsheet is shown in Figure 6 using 61 wt % nitric acid. After the waste cut, slightly dilute recycle nitric acid is added continuously while a mixed acid stream is distilled from the tank for return to the dissolution process. A second continuous addition is then made with recycle acid which has been prepared by blending acid produced in a previous cycle with fresh nitric acid.

Distillation of acid containing small amounts of chloride is continued after the second continuous addition is completed. This recycle acid stream is split into two parts, approximately half being used in the next run for the initial addition of recycle acid and the other half being blended with fresh 61% acid to prepare the second recycle addition. After the two continuous acid additions and distillation steps, dilution produces solvent extraction feed containing less than 350 ppm chloride.

Each basic flowsheet (Figures 5 and 6) has certain advantages and disadvantages. More elaborate tankage and instrumentation are required in the

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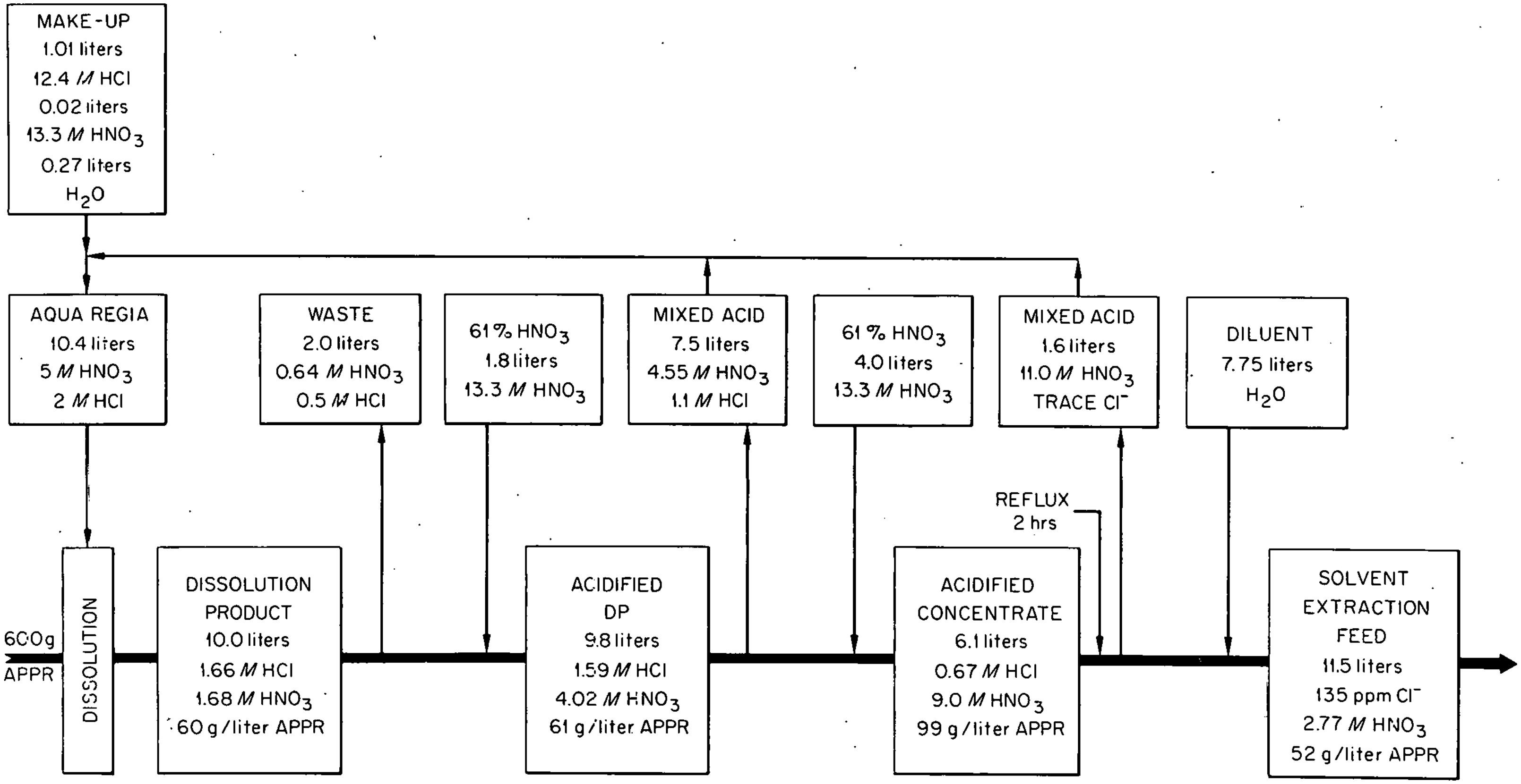

Fig. 5. The Darex Process: Reflux Flowsheet for Batchwise Operation Using 61 wt % HNO_3. Run No. APPR-31.

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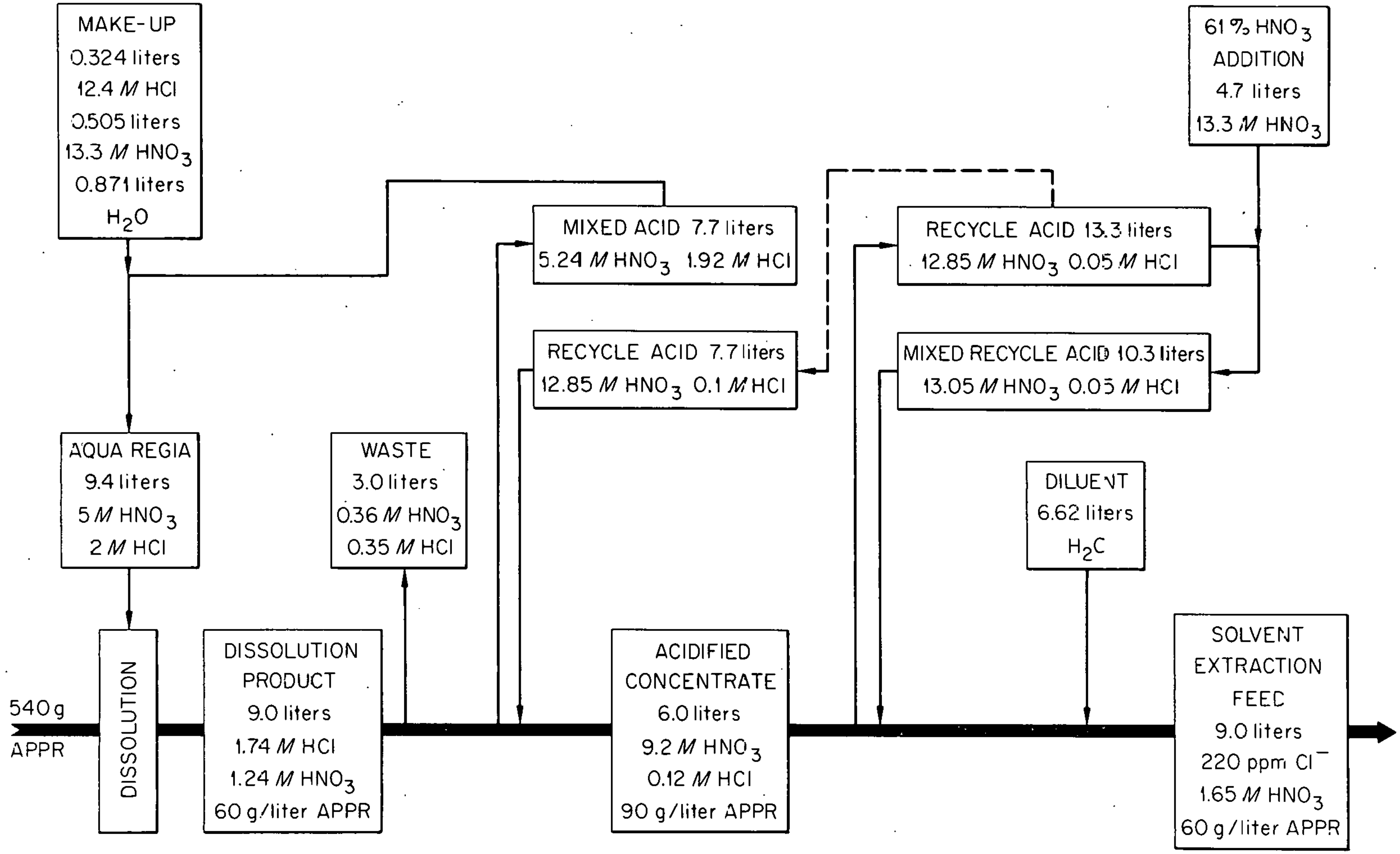

Fig. 6. The Darex Process: Recycle Flowsheet for Batchwise Operation Using 61% HNO_3. Run No. APPR-40.

case of the Recycle flowsheet. Consider, however, the tank to which recycle acid is added while mixed acid is removed continuously. A gradual increase in the acidity occurs with a gradual decrease in the chloride concentration. The chloride is removed first from a low acid stream, and as its concentration decreases its vapor pressure is maintained high by an increase in acidity. The converse is true during a Reflux batch distillation.

The salt concentration in a Recycle flowsheet is low throughout most of the process with two accompanying advantages. First, the amount of complexing of the chloride is minimized at low salt concentrations, and second there is little danger that the salt content could increase to saturation resulting in precipitation and scaling.

The major advantage of the Reflux flowsheet is that the period of refluxing may be varied in order to remove the last traces of chloride from the acidified concentrate. Laboratory studies indicate that chloride is removed by the refluxing operation for periods in excess of 6 hours. In addition the amount of chloride which is removed in the final distillation step can not influence the performance of subsequent Darex dissolutions and head-end treatments since all mixed acid is converted to 5/2 aqua regia. In the case of the Recycle flowsheet small amounts of chloride may build up in the final recycle loop, eventually resulting in off-specification solvent extraction feed.

The advantages of each basic concept have been combined in the so-called ORNL Reference flowsheet (see Figure 7). True countercurrent action is achieved in that only virgin 61% acid is added before the last chloride removal step. The recycle acid is distilled in a batch and collected for use in the next run. During the next run recycle acid is added continuously to the concentrated dissolution product, and mixed acid is distilled for aqua regia make-up in the third run. The operation of this flowsheet during run APPR-52 resulted in solvent extraction feed with the lowest chloride content of any previous runs, without the use of a sparge during the reflux step. Since this run more tests have been carried out (some without sparging or reflux) with final chloride concentration consistently on the order of 30 ppm.

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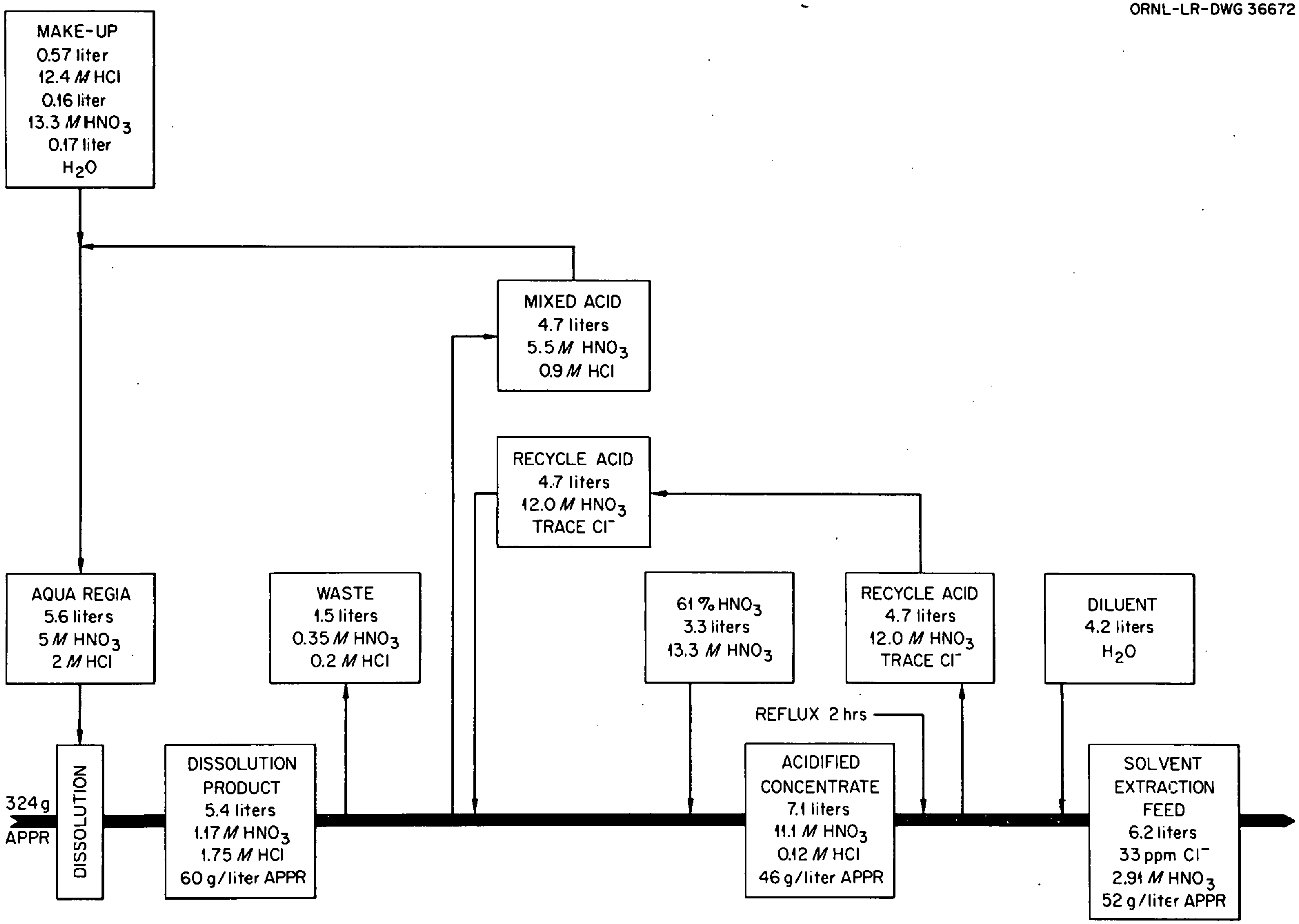

Fig. 7. The Darex Process: Reference Flowsheet for Batchwise Operation Using 61 wt % HNO_3. Run No. APPR-52.

The preliminary flowsheet of the ORNL Darex pilot plant is shown in Figure 8. It is planned to use a critically safe cylinderical dissolver. APPR-fuel elements may be added to the dissolver through the roof plugs, and a continuous dissolution process may be used to produce dissolver product which is collected in the feed adjustment tank. As the dissolution process continues, the fuel elements gradually move down the dissolver in a "melting icicle" operation.

All steps for chloride removal are carried out in the feed adjustment tank. Heat required for distillation is transferred through the jacketed connecting risers. During operation of the ORNL Reference flowsheet the first distillation process would remove a waste acid stream which would be collected in the neutralization tank. Approximately 12 molar nitric acid would then be added continuously to the feed adjustment tank while mixed acid is distilled and collected in the mixed acid catch tank.

A batch addition of 61% acid is then made directly to the feed adjustment tank or through the recycle acid tank. The feed adjustment tank may then be refluxed for several hours with condensate return through the recycle line. A final distillation of a concentrated nitric acid is then carried out and approximately 12 molar acid is collected in the concentrated acid tank.

Diluent water is then added to the feed adjustment tank, and the contents are jetted to the feed clarification tank. After filtration to remove dehydrated silica the clarified feed is pumped to solvent extraction or to storage.

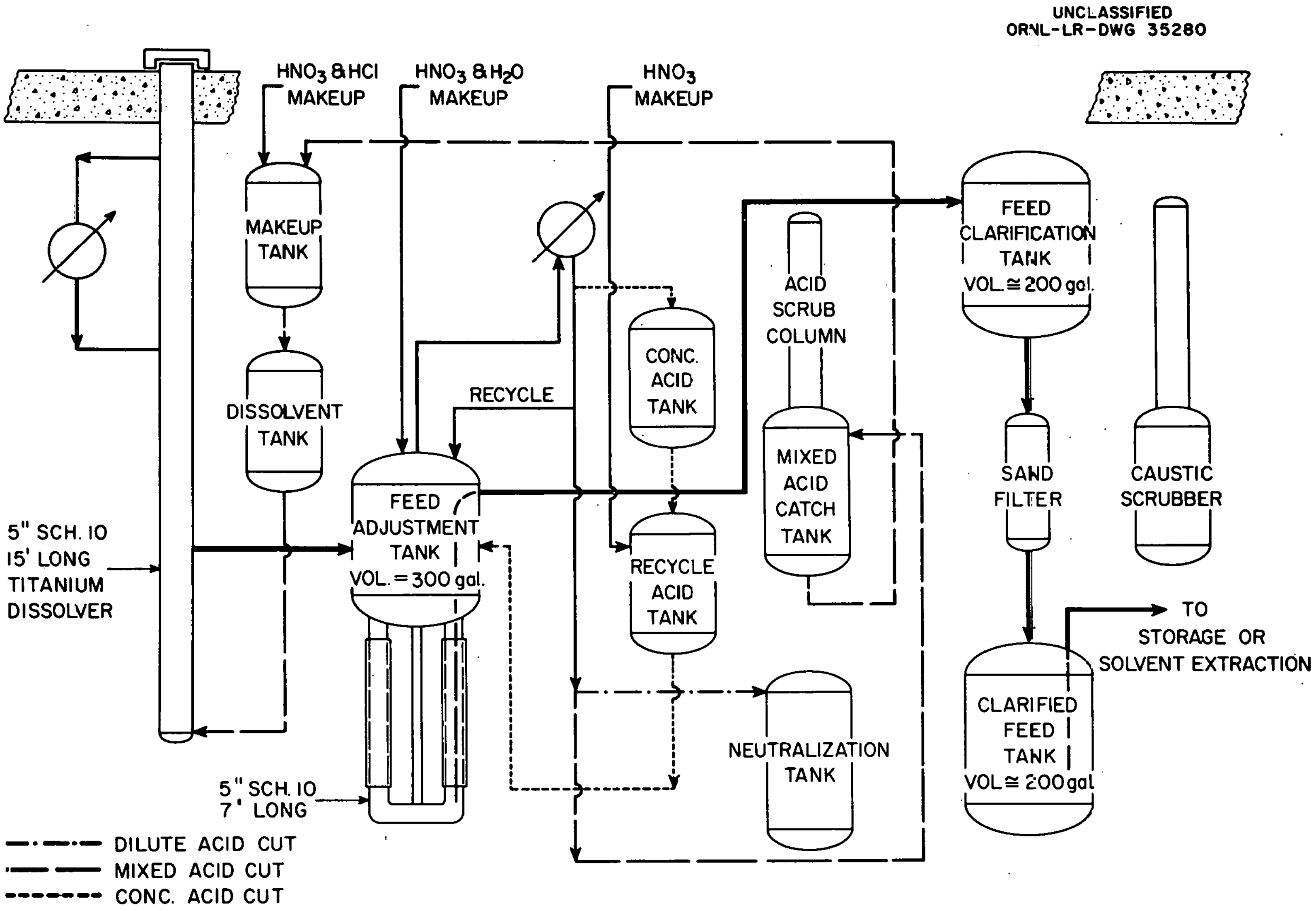

Fig. 8. Preliminary Flowsheet ORNL-Darex Pilot Plant.

Stainless Steel Jacket Dissolution in Dilute Sulfuric Acid (Sulfex Process). Dissolution of stainless steel jackets in dilute sulfuric acid followed by dissolution of the core in nitric acid has been proposed as a method for processing stainless steel clad-oxide core fuels (Sulfex process).(1,11,12) Data concerning dissolution rates and solubilities were also reported in these references. An example of this fuel type is the Consolidated Edison fuel rod which consists of a 30 mil 304L stainless steel jacket over a core containing pellets of 94.4% ThO_2-5.6% UO_2. Data for the flowsheet shown in Fig. 9 have been derived using unirradiated samples. The effects of high levels of radiation are unknown.

Removal of the 30 mil 304L stainless steel jacket is accomplished in 6 hr by dissolution in boiling 4 or 6 $\underline{M}$ H_2SO_4. Hydrogen is the only gaseous product. Use of 4 $\underline{M}$ acid is preferred, but evidence from experiments with irradiated fuel indicates that 6 $\underline{M}$ H_2SO_4 may be required to prevent passivation of the steel. The solids remaining after decladding consist of the stainless steel end caps and the ThO_2-UO_2 core pellets. Uranium and thorium losses to the decladding solution are about 0.02%. After the dissolver has been thoroughly rinsed with water to remove sulphate, about 95-98% of the core is dissolved in 7 hr in 13 $\underline{M}$ HNO_3-0.04 $\underline{M}$ NaF-0.04 $\underline{M}$ $Al(NO_3)_3$. The product solution, 1 $\underline{M}$ $Th(NO_3)_4$-8.5 $\underline{M}$ HNO_3, must undergo an evaporation for final acid adjustment prior to solvent extraction. After the core dissolution, the dissolver must again be thoroughly rinsed, preferably with a dilute solution of $Al(NO_3)_3$, to prevent contamination of the next decladding solution with fluoride and nitrate. After several cycles, the ThO_2-UO_2 heel and the undissolved stainless steel end caps will attain a steady-state amount.

Nionel stabilized with titanium appears to be the best of several materials of construction tested. The corrosion rate of Nionel in cyclic tests simulating the conditions shown in Fig. 9 was ~12 mils/yr as compared to ~18 mils/yr for Carpenter 20-Cb.

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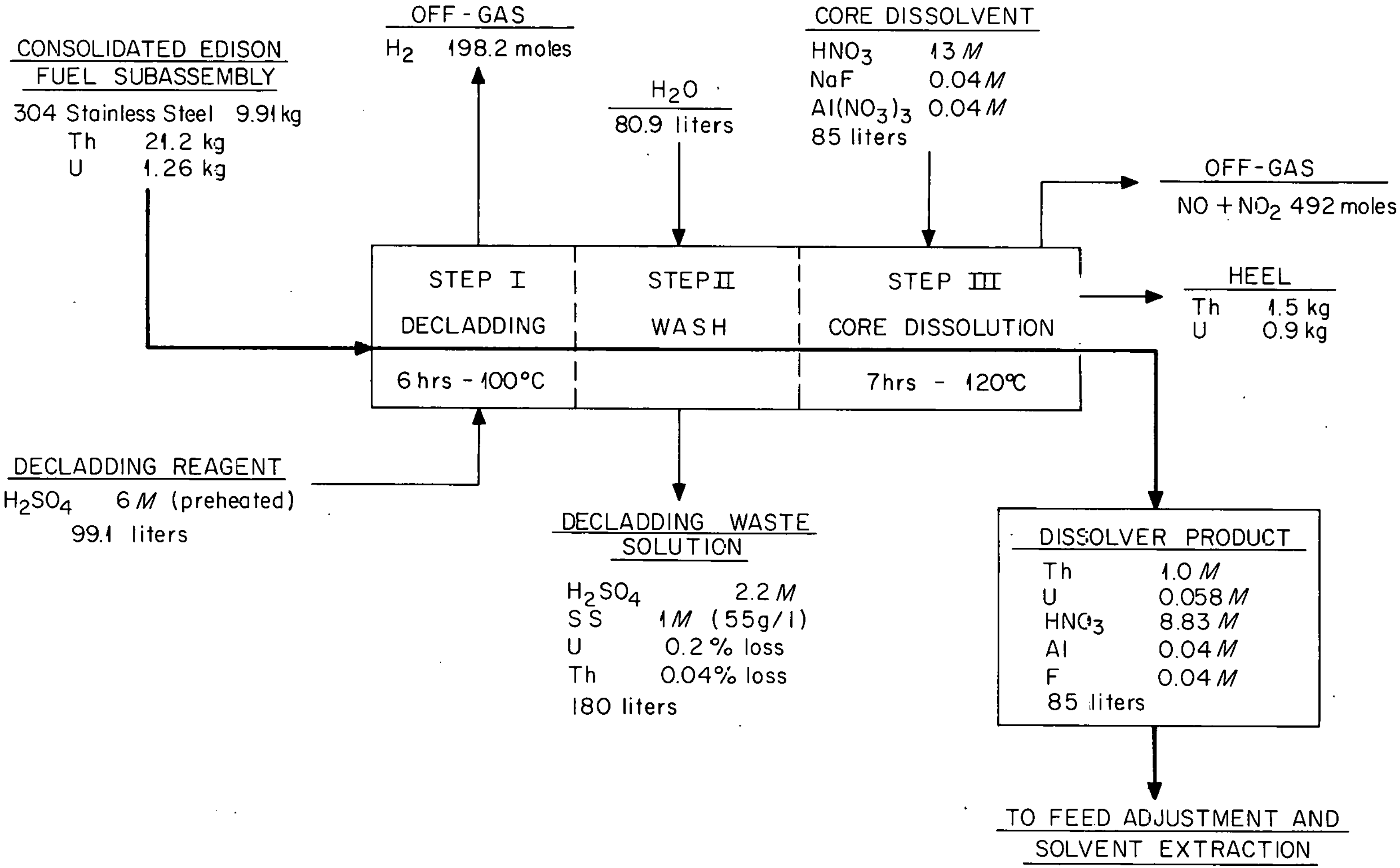

Fig. 9. Sulfex Process for Dejacketing Stainless Steel Jacketed Fuel In Dilute Sulfuric Acid.

Mechanical Processing

Introduction - Spent power reactor fuel elements may be prepared for dissolution and solvent extraction treatment by preliminary mechanical treatment. This mechanical treatment may vary from an extremely simple to a relative complex operation. An example of a simple disassembly procedure would be the removal of an end box or spider from a series of fuel bearing tubes by the removal of a retaining pin with remote manipulators. An example of a complex operation would be those procedures necessary to shear an entire fuel assembly into short sections which could be leached with nitric acid.

At Oak Ridge National Laboratory a development program is being carried out to determine the feasibility of various mechanical fuel reprocessing procedures. A large hot cell called the "Segmenting Facility" is under construction and plans have been made to install various types of equipment of sufficient versatility that their application to several different fuel types may be studied. At the end of the development program it is expected that a comparison may be made from the points of view of technical feasibility and economics of the two basic methods which have been proposed for solvent extraction feed preparation. These two methods are the use of chemicals alone and the use of a combination of mechanical and chemical treatment.

The Disassembly of SRE Fuel Elements - The present SRE fuel element (shown in Figure 10) consists of natural uranium slugs canned in stainless steel with an annular space filled with sodium potassium alloy and with an expansion volume at the top of the element filled with helium. Relatively simple mechanical treatment is possible to separate the stainless steel from the uranium, and the basic feasibility of such treatment was demonstrated in the SRE Hot Cell(13).

The procedure used at Canoga Park was to cut off one end of the element with an abrasive saw. If the slugs did not slide out by raising the uncut end, two additional cuts were made along the length of the element. However the experiment was preliminary since it was not expected that the fuel processing would be carried out at the reactor site.

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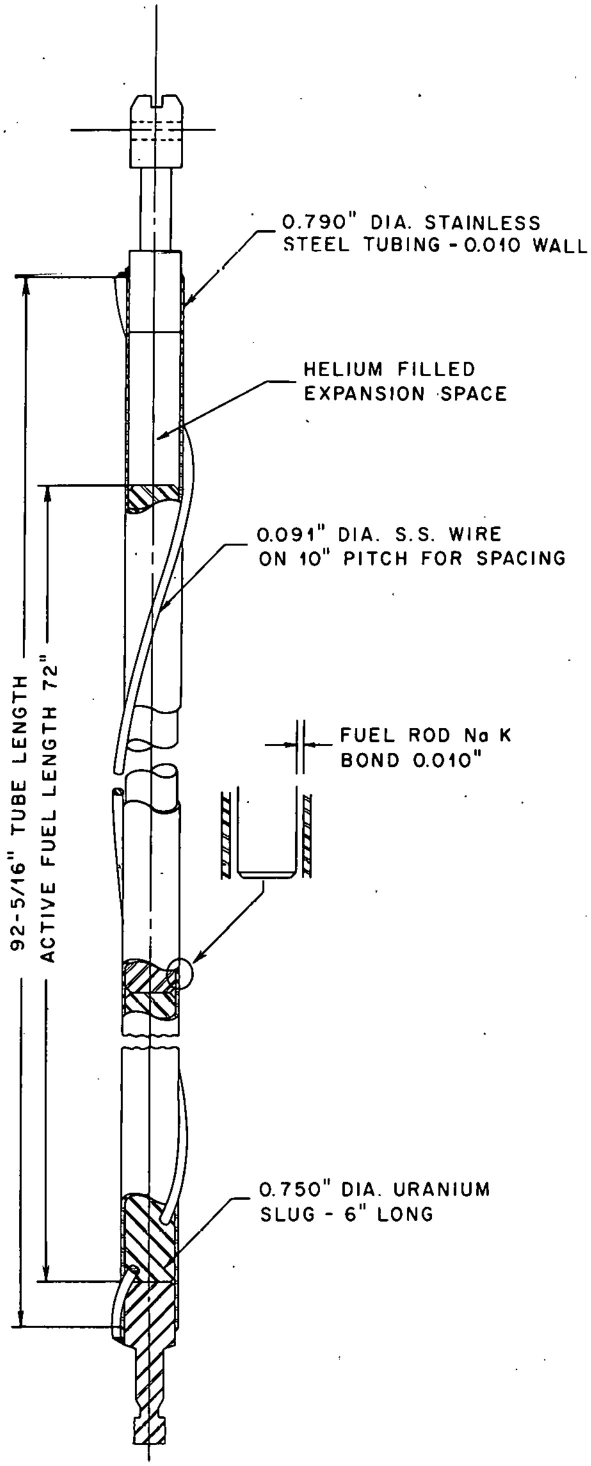

Fig. 10. SRE Fuel Element.

Equipment has been designed for installation in the segmenting hot cell at ORNL to remove the cladding from the SRE fuel(14). The entire mechanical processing equipment for the SRE fuel is shown in Figure 11. Since the fuel element itself is approximately 8 feet long and since one step in the processing procedure involved passing a shaft through the entire length of the fuel element, the overall length of the decladding equipment is approximately 20 feet. The important mechanical features are the end cap cutters (Nos. 10 and 16), the hydraulic wire cutter (No. 12), the shaft drive gear box and collet (No. 11), and the disposal winder system (Nos. 18, 19, and 21).

The steps in the decladding procedure are shown in Figures 12, 13, 14, and 15. The fuel element is wrapped with a stainless steel wire helix with a 10-in. pitch. The wire will be removed by a cable suspended hydraulic cutter which will break the wire every 10 inches (see Figure 12). The pieces of cut wire will be lifted from the kerosene tank by the remote manipulators.

The support rolls within the tank are then rotated while cutters are pressed against the stainless steel jacket to cut through the cladding only. The inert ends of the fuel may then be removed (see Figure 13).

A hydraulic ram incorporating an internal collet is used to push the element into an external collet, and both ends of the fuel element may be sealed. Kerosene at pressures up to 3000 psi can be pumped into the element to inflate the cladding and to increase the gap between the uranium slugs and the stainless steel tube. The internal collet can then be removed and the uranium slugs may either be flushed out with kerosene or pushed from the tubing with a tubular jack screw into the basket receiver (see Figure 14).

Finally, the empty cladding may be pressed at one end with a manipulator and fed to a slot in a reel. As the reel revolves the cladding is formed into a flat spiral roll approximately 3 inches in diameter (see Figure 15). This roll will be canned for removal from the hot cell and burial. The slugs are cleaned, canned in aluminum, and transported in a carrier to the Power Reactor Fuel Reprocessing Pilot Plant for dissolution and solvent extraction. The nominal capacity of the decanning equipment is 300 kg U/day.

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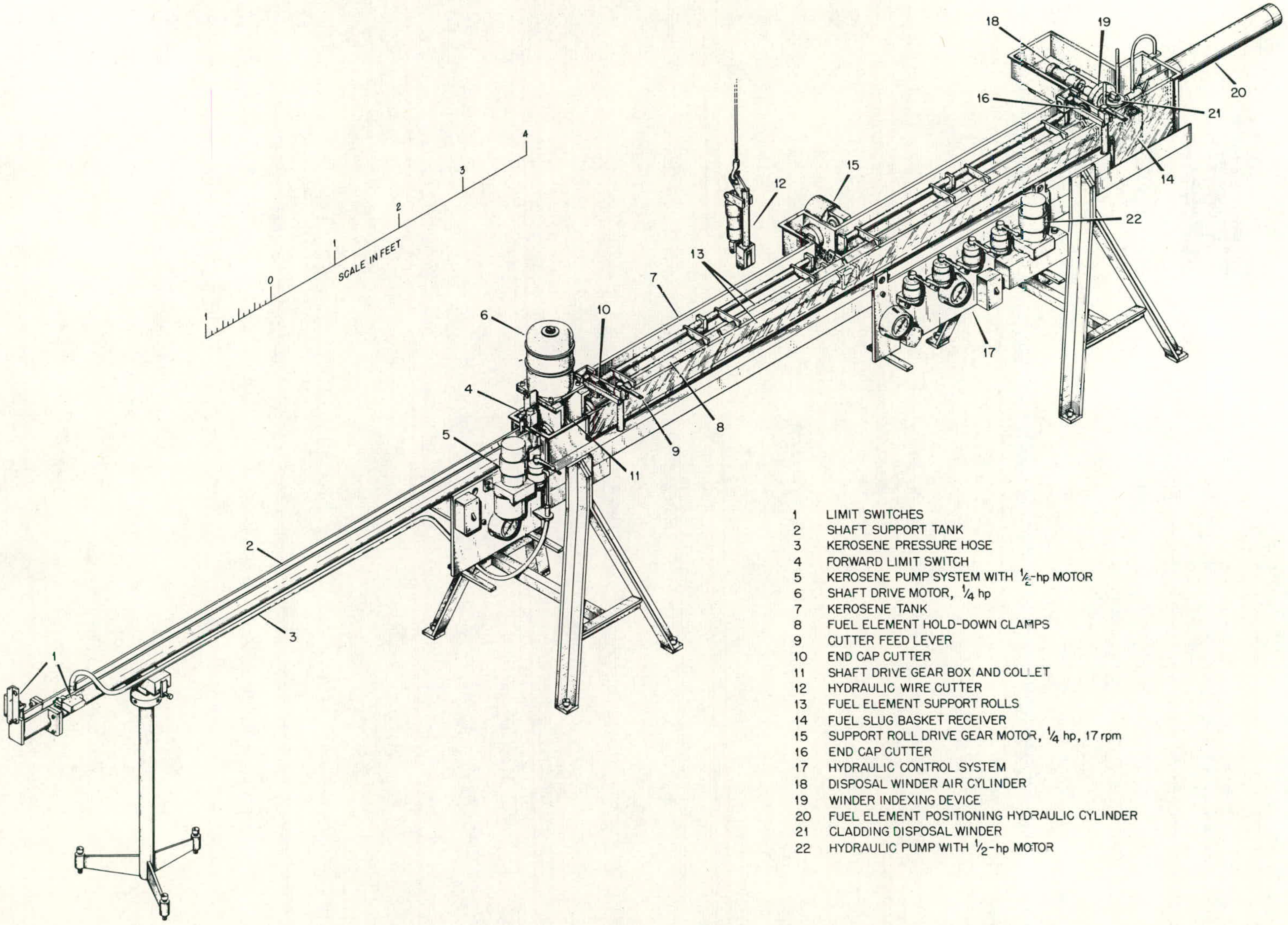

1	LIMIT SWITCHES
2	SHAFT SUPPORT TANK
3	KEROSENE PRESSURE HOSE
4	FORWARD LIMIT SWITCH
5	KEROSENE PUMP SYSTEM WITH 1/2-hp MOTOR
6	SHAFT DRIVE MOTOR, 1/4 hp
7	KEROSENE TANK
8	FUEL ELEMENT HOLD-DOWN CLAMPS
9	CUTTER FEED LEVER
10	END CAP CUTTER
11	SHAFT DRIVE GEAR BOX AND COLLET
12	HYDRAULIC WIRE CUTTER
13	FUEL ELEMENT SUPPORT ROLLS
14	FUEL SLUG BASKET RECEIVER
15	SUPPORT ROLL DRIVE GEAR MOTOR, 1/4 hp, 17 rpm
16	END CAP CUTTER
17	HYDRAULIC CONTROL SYSTEM
18	DISPOSAL WINDER AIR CYLINDER
19	WINDER INDEXING DEVICE
20	FUEL ELEMENT POSITIONING HYDRAULIC CYLINDER
21	CLADDING DISPOSAL WINDER
22	HYDRAULIC PUMP WITH 1/2-hp MOTOR

Fig. 11. Mechanical Decladding Equipment for SRE (NaK Bonded) Fuel Elements.

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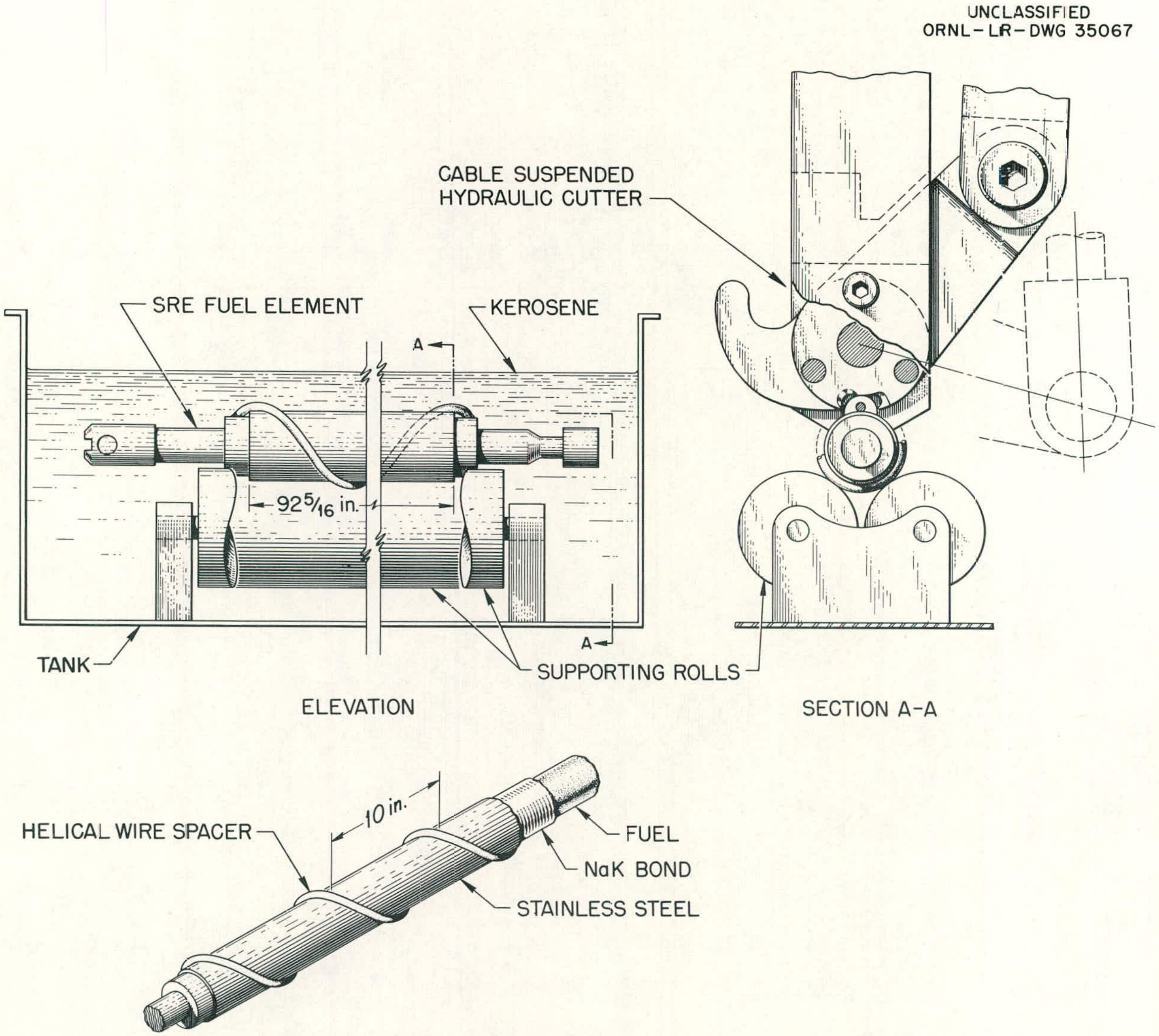

Fig. 12. Fuel Element is Placed on Supporting Rolls and Helical Wire Spacer is Cut Off at Both Ends and at 10-in. Lengths for Disposal.

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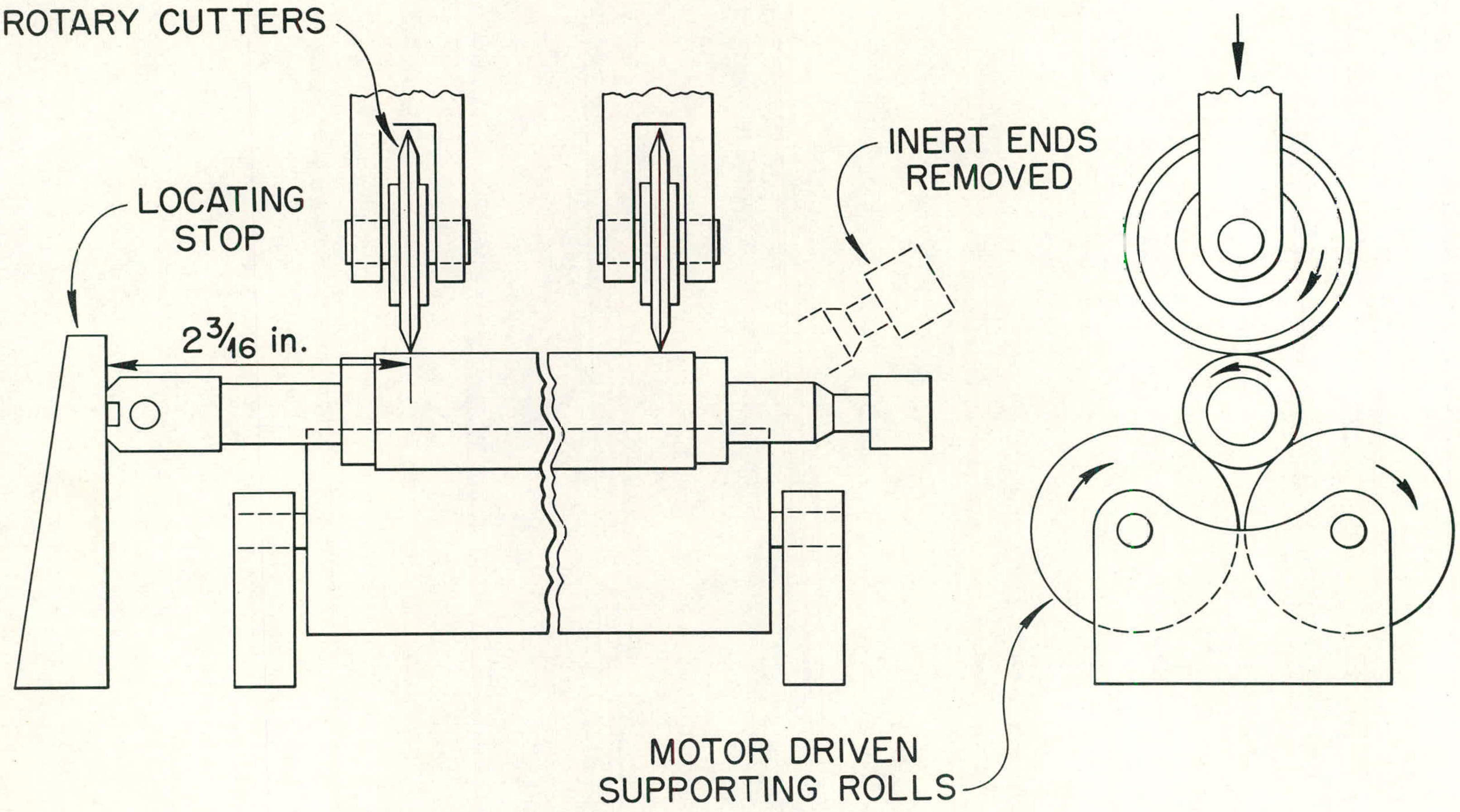

Fig. 13. Supported Rolls are Rotated While Rotary Cutters Cut Through Cladding Only. Inert ends are removed.

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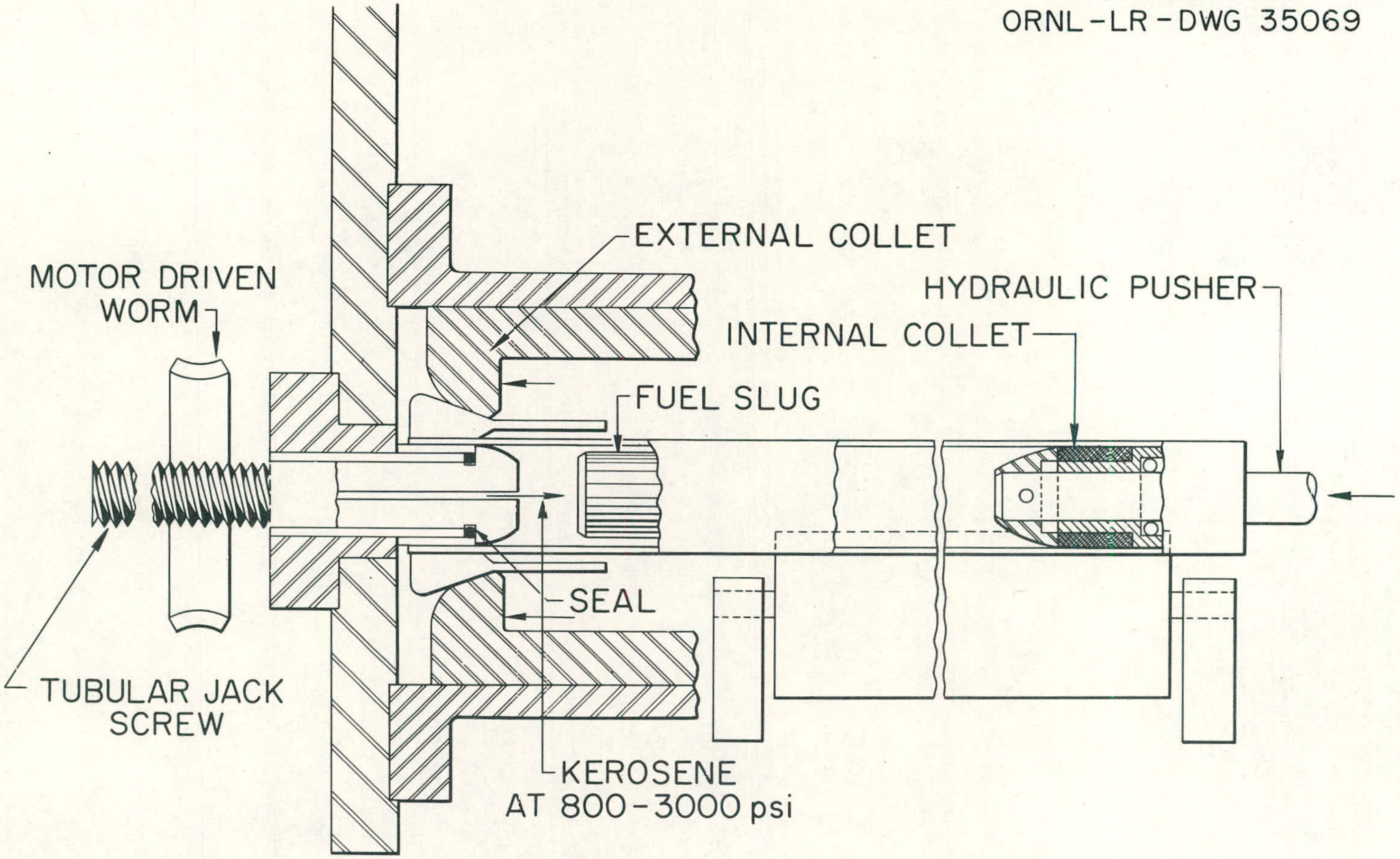

Fig. 14. Hydraulic Pusher Propels Fuel Element into External Collet. Kerosene at 800-3000 psi can be used to inflate the cladding. With the internal collet removed, the slugs may be flushed out with kerosene or ejected with the tubular jack screw into the basket receiver provided.

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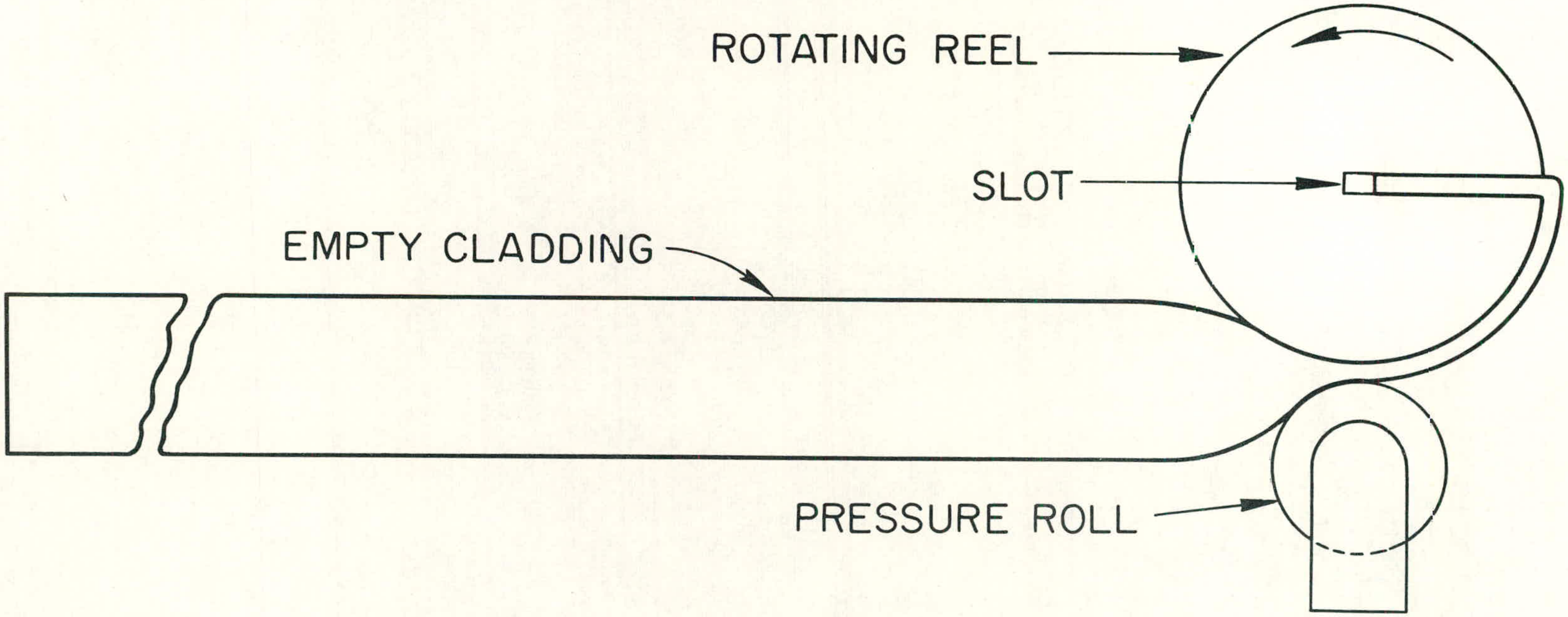

Fig. 15. One End of the Empty Cladding is Flattened by GM Manipulator and Placed into the Slot of a Rotating Reel. As the reel revolves, the cladding is formed into a flat spiral package approximately 3 in. in diameter.

The Development of Chopping and Leaching Procedures - A more complicated fuel design from the point of view of mechanical processing is one in which ceramic pellets are enclosed in stainless steel or zirconium tubes and the tubes are assembled in a box-like structure. Examples of fuels of this type are those for the PWR blanket, the Commonwealth Edison, the Yankee, and the Nuclear Ship Savannah reactors. It may be possible to shear the entire fuel assemblies and leach the acid soluble cores. However, as a preliminary treatment, it has been proposed that the box-like structures be reduced to individual tubes or layers of tubes. Shearing and leaching of single fuel rods has been shown to be feasible in previous studies(15).

Two methods of reducing a fuel assembly are shown in Figures 16 and 17. In Figure 16 a ferrule splitting tool is shown through which a fuel bundle may be forced after the removal of end boxes. A series of splitting knives pass between the fuel pins and cut the small tubular ferrules which hold the fuel bundle together. In Figure 17 a different concept is shown in which a knife is passed between the layers of fuel pins to split the ferrules and to reduce the bundle to slabs or layers of tubes. These slabs may then be sheared on a 45° angle to avoid the problem of several pins being held together by split ferrules and also to increase the surface area available for leaching.

The various pieces of mechanical dismantling equipment which will be installed in the segmenting facility in Building 3026 at ORNL are shown in the next three figures. Figure 18 is a plan view of the segmenting facility. A typical fuel bundle is mounted on a transversing table and passed under a disc saw for the removal of inert end boxes. The same transversing table can be used to pass the fuel bundle through dies to split the ferrules. However, an entire fuel bundle is shown being fed to a shear. Notice the SRE decladding equipment installed beside the transversing table.

In Figure 19 the equipment in the dismantling cell is shown in its relationship to the overhead manipulators. Not shown in either of the two drawings are the Argonne remote manipulators which are mounted at each of the three windows through the five foot shielding which surrounds the cell.

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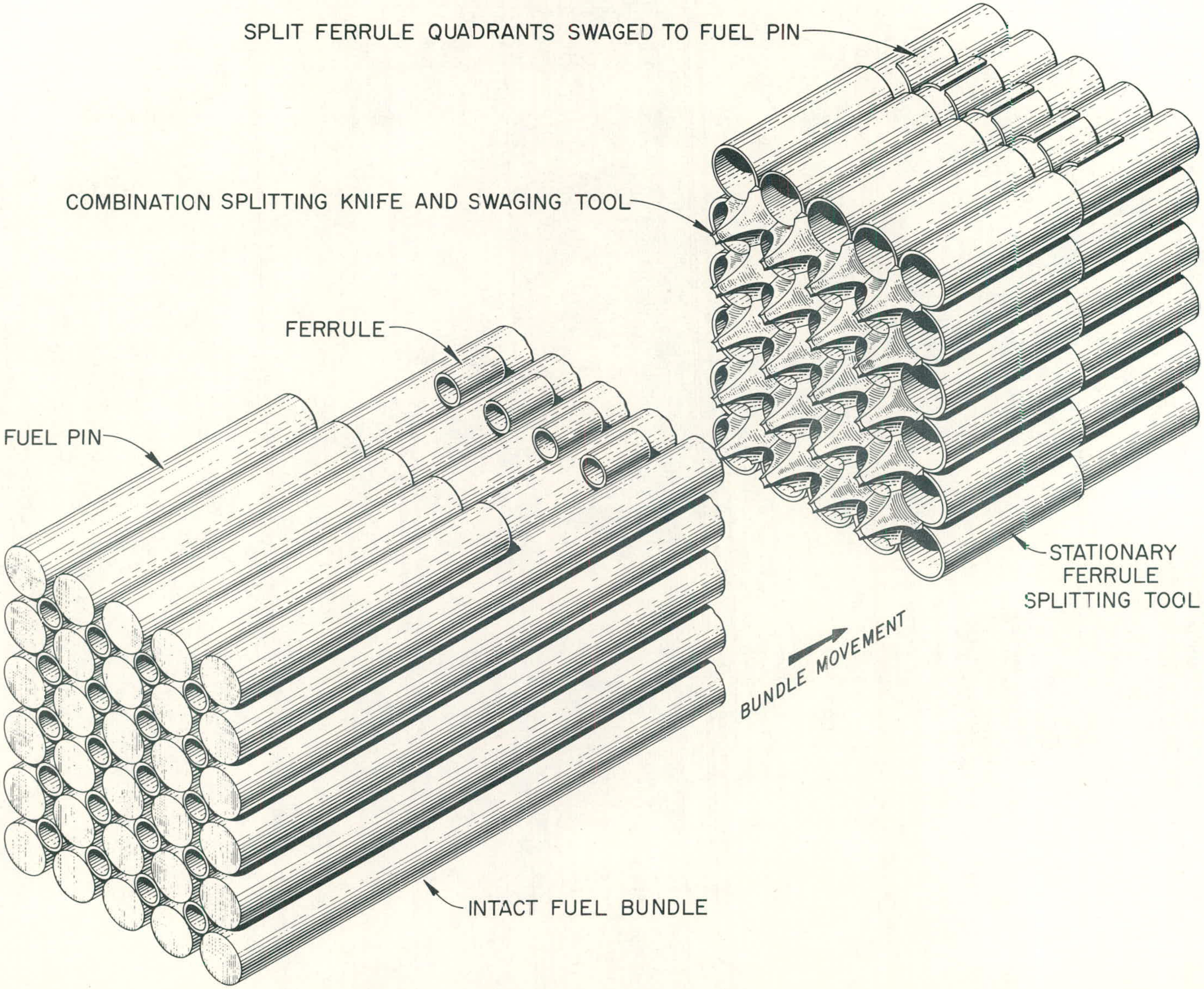

Fig. 16. Ferrule Splitting Tool for Separating Individual Tubular Elements from a Fuel Assembly.

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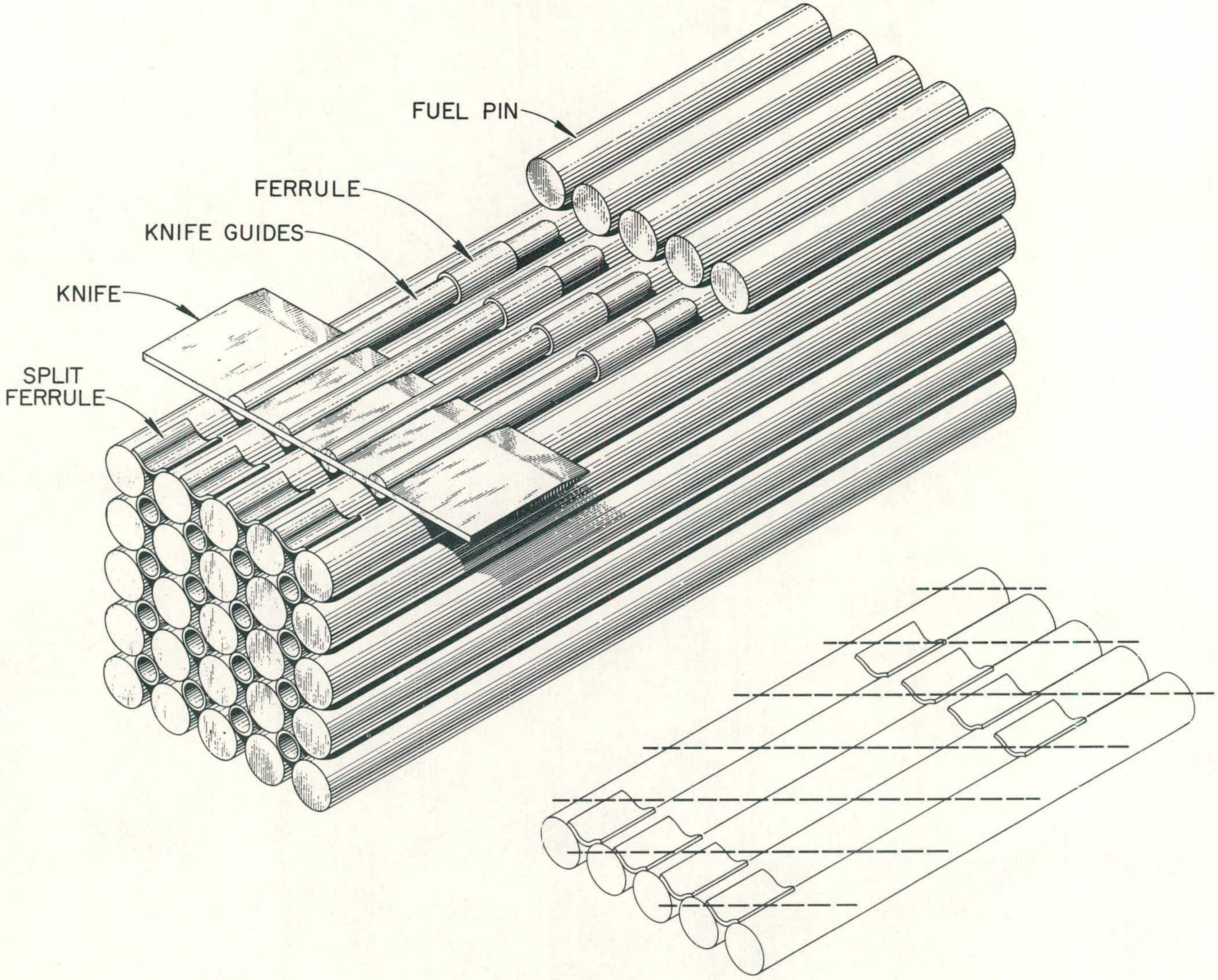

Fig. 17. Ferrule Splitting Tool for Separating Slabs of Tubular Elements from a Fuel Assembly.

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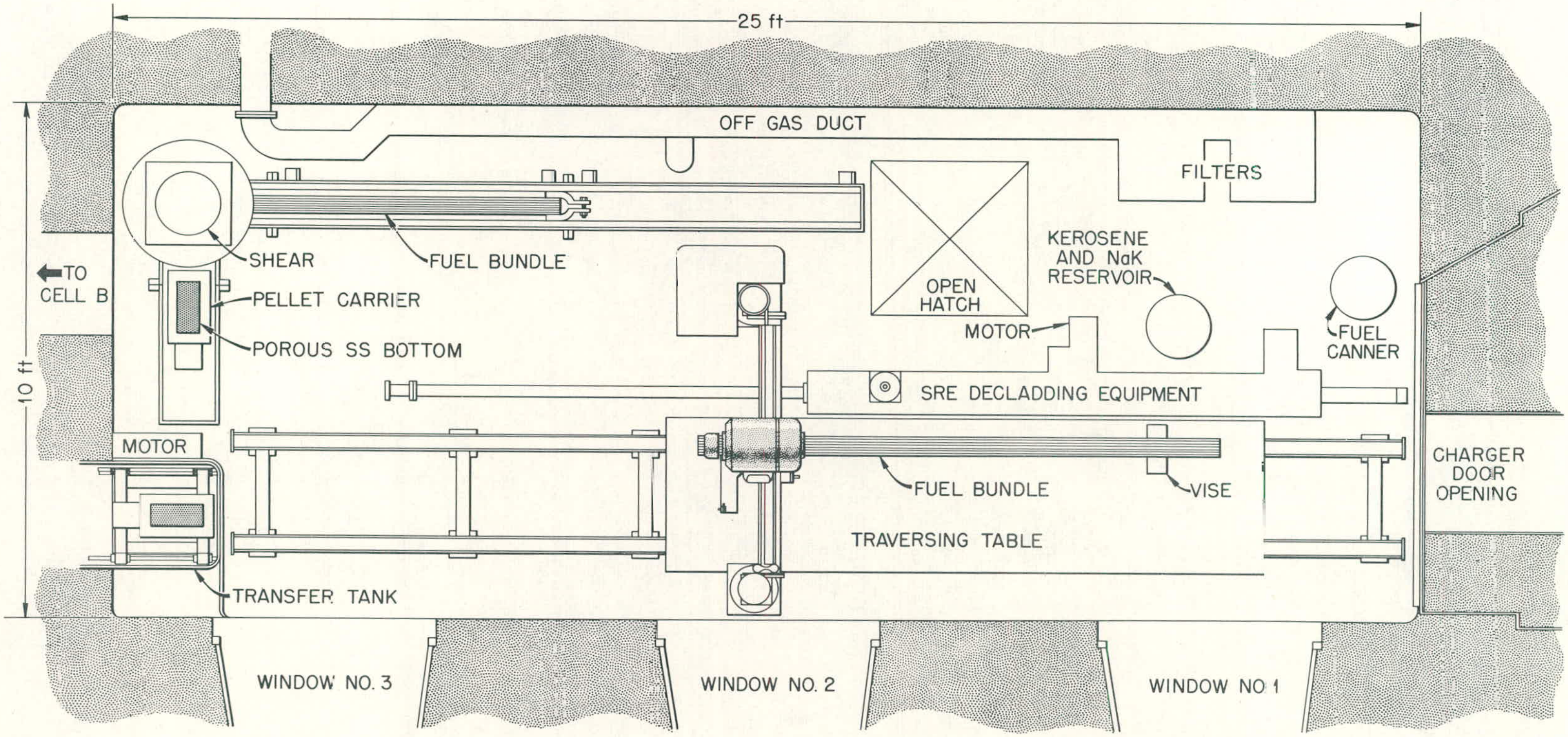

Fig. 18. Proposed Installation in Segmenting Facility – Bldg. 3026 Plan View – Cell "A" (Dismantling and Shearing).

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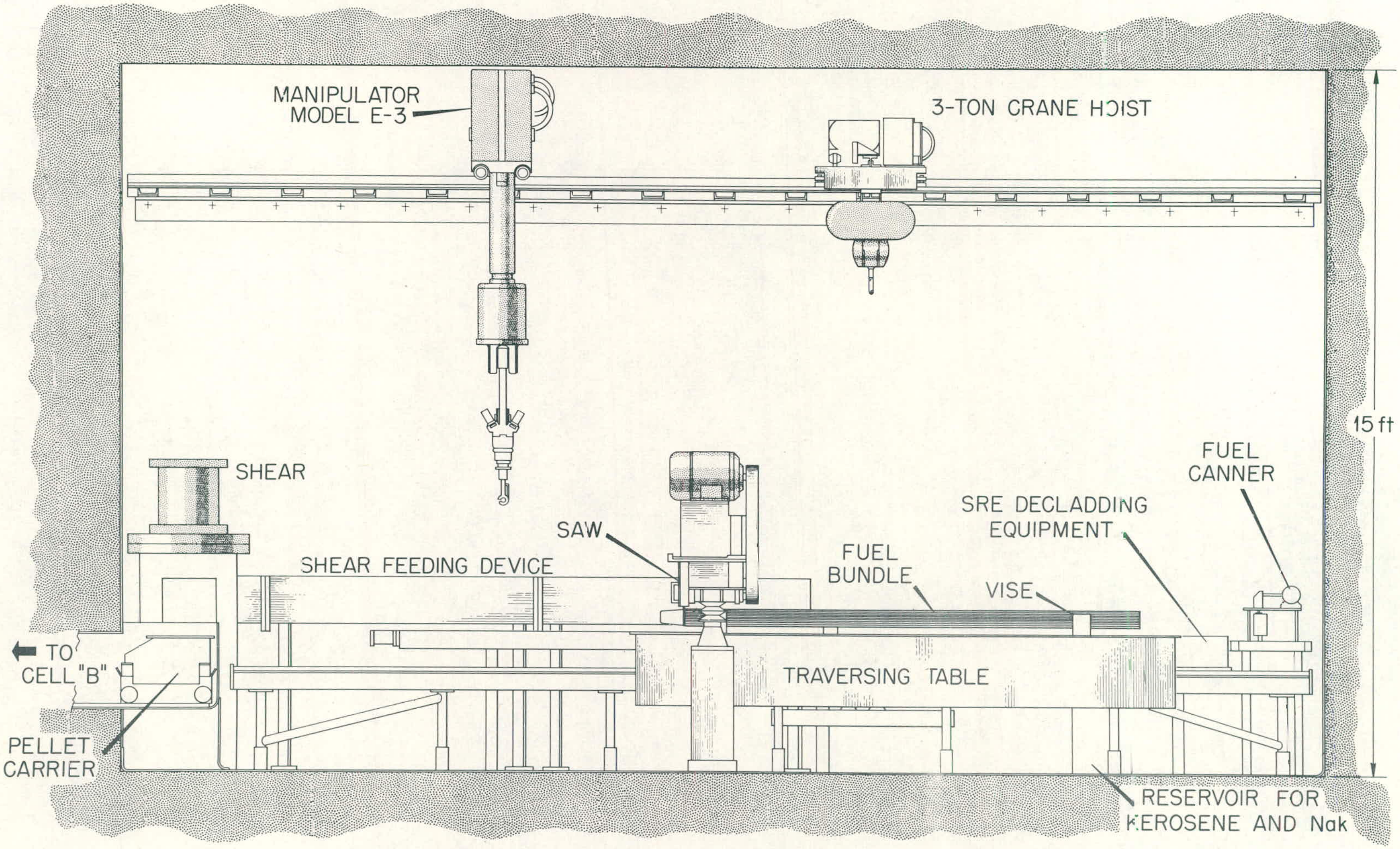

Fig. 19. Proposed Installation in Segmenting Facility - Bldg. 3026 Front Elevation - Cell "A" (Dismantling and Shearing).

The leaching cell in the segmenting facility is shown in Figure 20. Pieces of sheared fuel assemblies which are collected in some type of pellet carrier (in the case illustrated, a slab-shaped carrier is shown) may be passed from the dismantling and shearing cell into the leaching cell through a water-filled transfer tank. An overhead crane would be used to move the pellet carrier from the transfer tank to the leacher. One possible leach dissolver design is illustrated, but a more feasible design would consist of a slab acid tank and critically safe cylindrical leach vessels connected to the tank. A porous stainless steel top and bottom on the pellet carrier could contain the chopped fuel while acid passes from the acid tank through the leach tank. If porous sides are provided for the pellet transfer carrier, the acid level could be maintained below the top of the carrier and a complete enclosure would not be necessary.

The leached inert solids could be discharged either by pouring the pellet carrier contents into a disposable can after leaching or by discarding the carrier. To minimize contamination problems it may be necessary to contain the pellet carrier in a light weight aluminum can at various steps in the processes.

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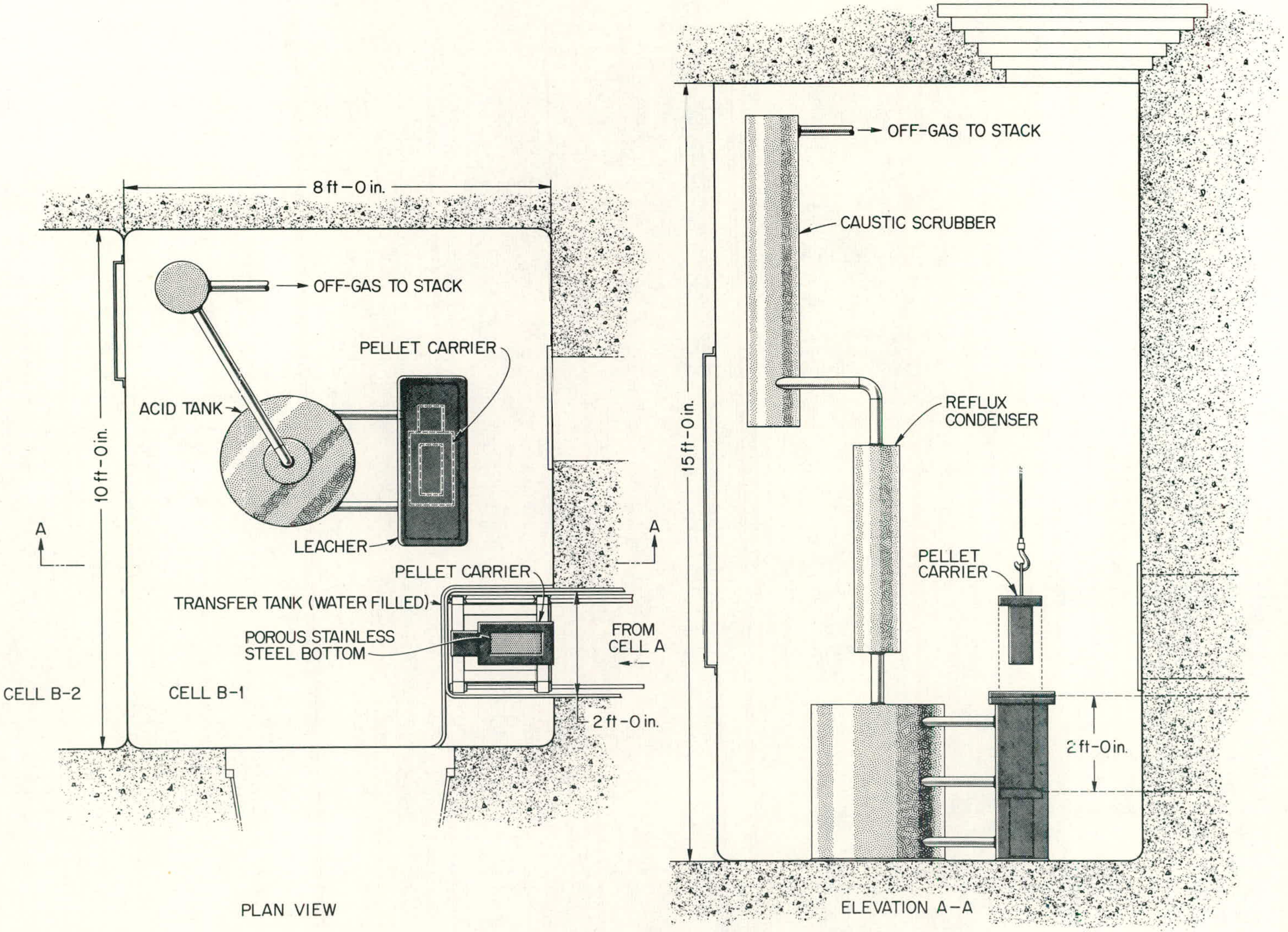

PLAN VIEW

ELEVATION A–A

Fig. 20. Proposed Installation in Segmenting Facility – Bldg. 3026 Plan and Elevation View – Cell "B" (Leach Facility).

SOLVENT EXTRACTION

Foreign Research Reactor Fuel Reprocessing

Foreign Research Reactor fuel consists of uranium-aluminum alloy plates clad with aluminum and brazed into a box assembly with an over-all composition of 84% Al, 15% U (20% enriched), and 1% Si. The TBP-25 process(16) previously developed for uranium-aluminum alloy fuels, was modified to incorporate an improved feed clarification procedure and to provide for the separation and ultimate recovery of plutonium(17) (Fig. 21).

Dissolution. Dissolution of uranium-aluminum alloy proceeds rapidly and smoothly in mercury-catalyzed nitric acid. The solvent extraction flowsheet specifies a feed composition of 1.2 $\underline{M}$ $Al(NO_3)_3$-1 $\underline{M}$ HNO_3. Tests with prototype FRR fuel plate showed that dissolution with 7.5 $\underline{M}$ HNO_3-0.005 $\underline{M}$ $Hg(NO_3)_2$ yields a dissolver solution containing 1.5 $\underline{M}$ $Al(NO_3)_3$ and 1.3 $\underline{M}$ HNO_3. With the dilution which occurs in the subsequent steps, i.e., feed clarification and plutonium valence adjustment, the desired feed concentration for solvent extraction is reached without further adjustment.

Feed Clarification. Large quantities of hydrous, colloidal silica are formed during dissolution which cause the formation of severe emulsions when the feed solution is solvent extracted. Dehydration of colloidal silica to an inactive form may be accomplished by extended reflux at high acidity; however, these conditions are corrosive to process equipment.(16) A more attractive alternative is to remove the silica from the system by treatment with gelatin.(18)

Approximately 100 mg of gelatin is added per liter of dissolver solution and the mixture digested at 85°C for 1 hr. A gelatin-silica polymer forms which can be removed by filtration or centrifugation. Occluded uranium and plutonium are readily washed from the filter cake with 0.1 $\underline{M}$ HNO_3. Feed solutions treated in this manner showed satisfactory phase separation times of 20 sec with 6% TBP-Amsco solvent. The gelatin-silica polymer is not particularly sensitive to radiation. Irradiation of gelatin-dissolver solution mixtures to the 2 and 4

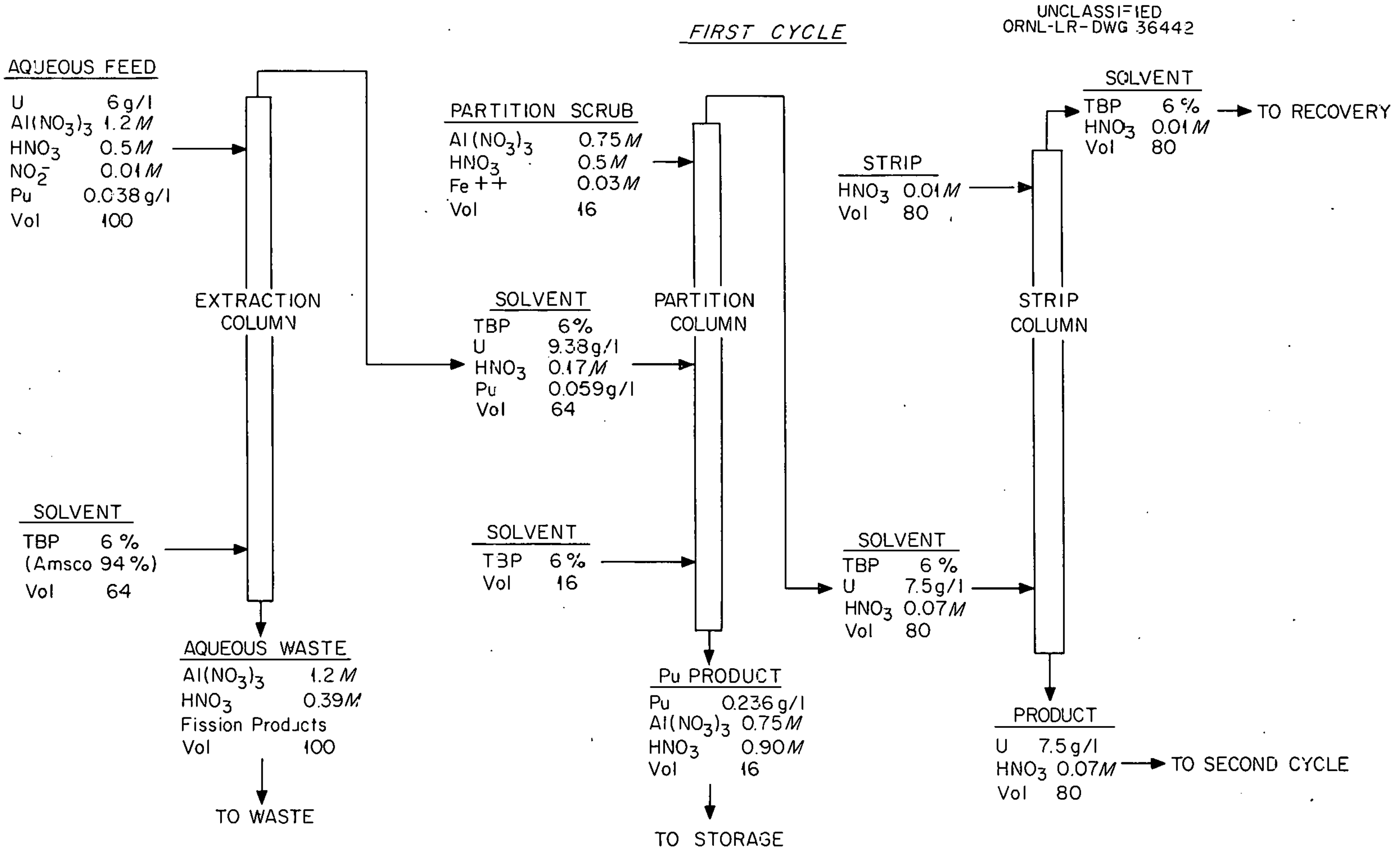

Fig. 21. Solvent Extraction Flowsheet for Foreign Research Reactor Fuel.

watt-hr/liter level, 2.5 to 5 times that expected in process conditions, produced no change in the solvent-aqueous phase settling time after filtration.

Sand Bed Filtration. Tests with gelatin-treated dissolver product established 30 mesh Ottawa sea sand as optimum filter media. Finer mesh sand gave rise to prohibitively low flow rates and plugging and coarser sand did not completely clarify the solutions. Instantaneous gravity flow rates were determined as a function of total throughput for 1.5 and 2.75 in. dia sand filters containing 10 in. deep beds of 30 mesh Ottawa sea sand (Fig. 22). In the absence of filter aid, the flow rate is rapid initially but drops quickly to <1 ml/min/cm^2. The addition of Johns-Manville #545 Celite filter aid, one to two g per liter of solution, increased and maintained the flow rate at acceptable values of 1-2 ml/min/cm^2 for three to six liters of solution.

Regeneration of the sand bed is accomplished by backwashing the filter cake with several volumes of water. The filter cake should not become dry before backwashing. Upon drying, the cake becomes compacted and lumpy, and is difficult to wash off the bed. Vacuum filtration also causes compaction. While wet, the filter cake is light and flocculent and easily slurried away from the relatively heavy particles of 30 mesh sand.

Criticality Control by Internal Neutron Poisons. The use of boron as an internal neutron poison has been considered as a means of criticality control. Tests showed that boron, 0.05 M boric acid in the dissolvent, will remain in solution through dissolution, gelatin treatment, filtration, and final feed adjustment. Upon extraction of the feed, boron is not extracted and is lost to the aqueous waste stream from the 1st column. Each column in the first solvent extraction cycle may be effectively poisoned, if desired, by adding boron to the aqueous streams entering the top of each column.

Solvent Extraction. A solvent composition of 6% TBP in Amsco diluent and an aqueous composition of 1.0 M $Al(NO_3)_3$ and 0.5 M HNO_3 was chosen

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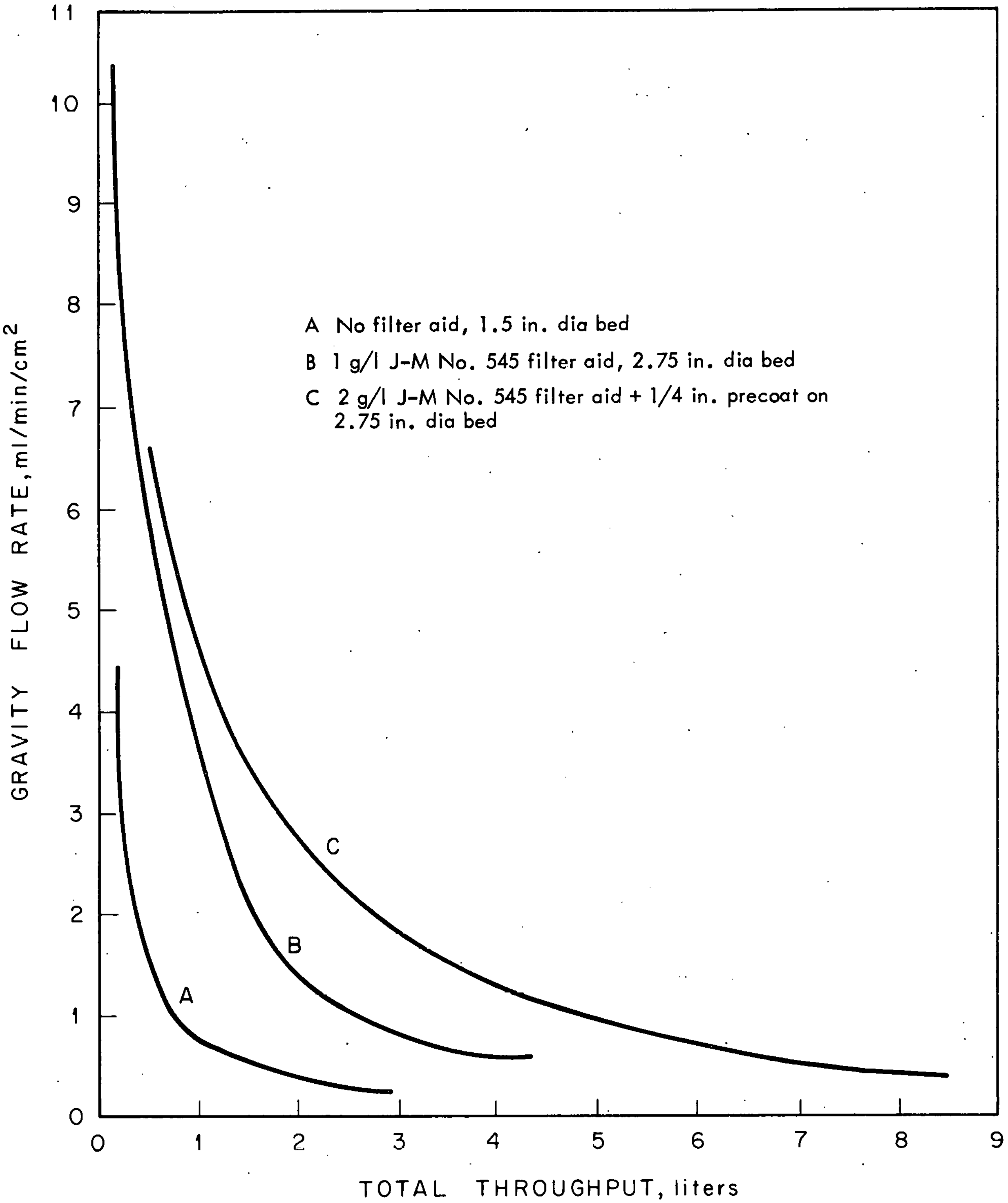

Fig. 22. Filtration of Gelatin-Treated Foreign Reactor Dissolver Product Through 10 in. of 30 Mesh Ottawa Sand; 6 in. Height of Liquid Over Bed.

for the 1st cycle of solvent extraction to obtain the maximum extraction efficiency consistent with criticality control. The uranium distribution coefficient, E_a^o, is about 10 times higher for 6% TBP than for 2.5% TBP (Table 2). Nitrite is added to convert plutonium to Pu(IV). The E_a^o for Pu(IV) is 7.6 under these conditions, which assures complete recovery of plutonium in the extraction column (Fig. 21). In the partition column, the remaining fission products and plutonium are removed from the organic phase by an aqueous scrub stream containing 0.03 M $Fe(NH_2SO_3)_2$, 0.75 M $Al(NO_3)_3$, and 0.5 M HNO_3. The ferrous ion reduces Pu(IV) to Pu(III), a form not readily extracted by TBP. The presence of aluminum ensures the extraction of uranium. The use of pure nitric acid as a scrub solution was unsuccessful. The distribution coefficients for uranium and plutonium under flowsheet conditions were 1.15 and 0.04, respectively, but decreased to 0.05 and 0.003 in the absence of aluminum.

Table 2. Effect of Acidity and TBP Concentration on Uranium Extraction

Feed: 5.2 mg U/ml, 1 M $Al(NO_3)_3$, varying HNO_3
Solvents: 2.5 and 6% TBP in Amsco 125-82
Equal volume equilibrations

Feed Acidity M	Uranium Distribution Coefficient, E_a^o 2.5% TBP	6% TBP
0.5	2.74	20.0
1.0	2.43	17.1
2.0	1.79	12.0
4.0	1.04	6.1

Solutions prepared by dissolution of unirradiated prototype Foreign Research Reactor Fuel and containing plutonium tracer were treated with gelatin, filtered through sand, and successfully processed in 0.75 in. pulse columns. All aqueous streams contained 0.05 M H_3BO_3 to aid in criticality control. Uranium losses to the aqueous waste, plutonium product, and stripped solvent streams using 22 feet of extraction column, 6 feet of back extraction in the partitioning column, and 11 feet of stripping column, were less than 0.001, 0.001, and 0.002%, respectively. Plutonium losses, were 0.03% to the aqueous waste and $\ll$ 1% to the uranium-bearing solvent from the partitioning column using 8 feet of partitioning section in this column.

Recovery of Uranium 233

A tentative solvent extraction flowsheet has been developed in laboratory scale equipment(19) for the recovery of uranium from ThO_2-UO_2 fuels as exemplified by the Consolidated Edison concept. The uranium will be a mixture of U-233 and U-235 since the fuel will contain fully enriched uranium initially. A decontamination factor of about 5×10^8 is required for the irradiation levels anticipated, i.e., approximately 10,000 Mwd/T of thorium after a decay of 6 months. Under present plans the thorium will not be recovered but will be stored with the fission products as a waste solution.

The process consists of two cycles (Fig. 23). The dissolver product, 1 $\underline{M}$ Th-0.035 $\underline{M}$ U-8.0 $\underline{M}$ HNO_3-0.04 $\underline{M}$ F-0.04 $\underline{M}$ Al (see Sulfex above), is combined with the raffinate from the 2nd cycle and evaporated to a B. P. of 140°C to remove the excess acid. The concentrate, 2.2 $\underline{M}$ Th-3.2 $\underline{M}$ Al-0.08 $\underline{M}$ F, is diluted with water to form the feed for the 1st cycle of extraction. The uranium is extracted with 2.5% tributyl phosphate in Amsco diluent and the uranium stripped from the solvent with 0.008 $\underline{M}$ $Al(NO_3)_3$. Phosphate is frequently added to the scrub solution to improve the separation from zirconium(20) but cannot be used in this case without exceeding the solubility of zirconium phosphate. The concentration of fission product zirconium will be very high, i.e., 0.02 $\underline{M}$ in the feed solution because of the high burn-up anticipated.

The first cycle product is adjusted for use as 2nd cycle feed by the addition of acid deficient aluminum nitrate. Sulfite is also added to improve the separation from ruthenium. Sulfite is effective in increasing the separation from ruthenium under acid deficient conditions but is not effective in the acidic conditions present in the first cycle.(20) Again phosphate cannot be used since the raffinate is recycled to the 1st cycle. The low acidity and high solvent saturation, i.e. 80% saturation, in the 2nd cycle are conducive to high separation from zirconium and rare earths, respectively. The flow rates are adjusted to assure a recycle of about 5% of the uranium from the 2nd to the 1st cycle, thus assuring high solvent saturation.

Laboratory countercurrent batch extractions, using flowsheet conditions

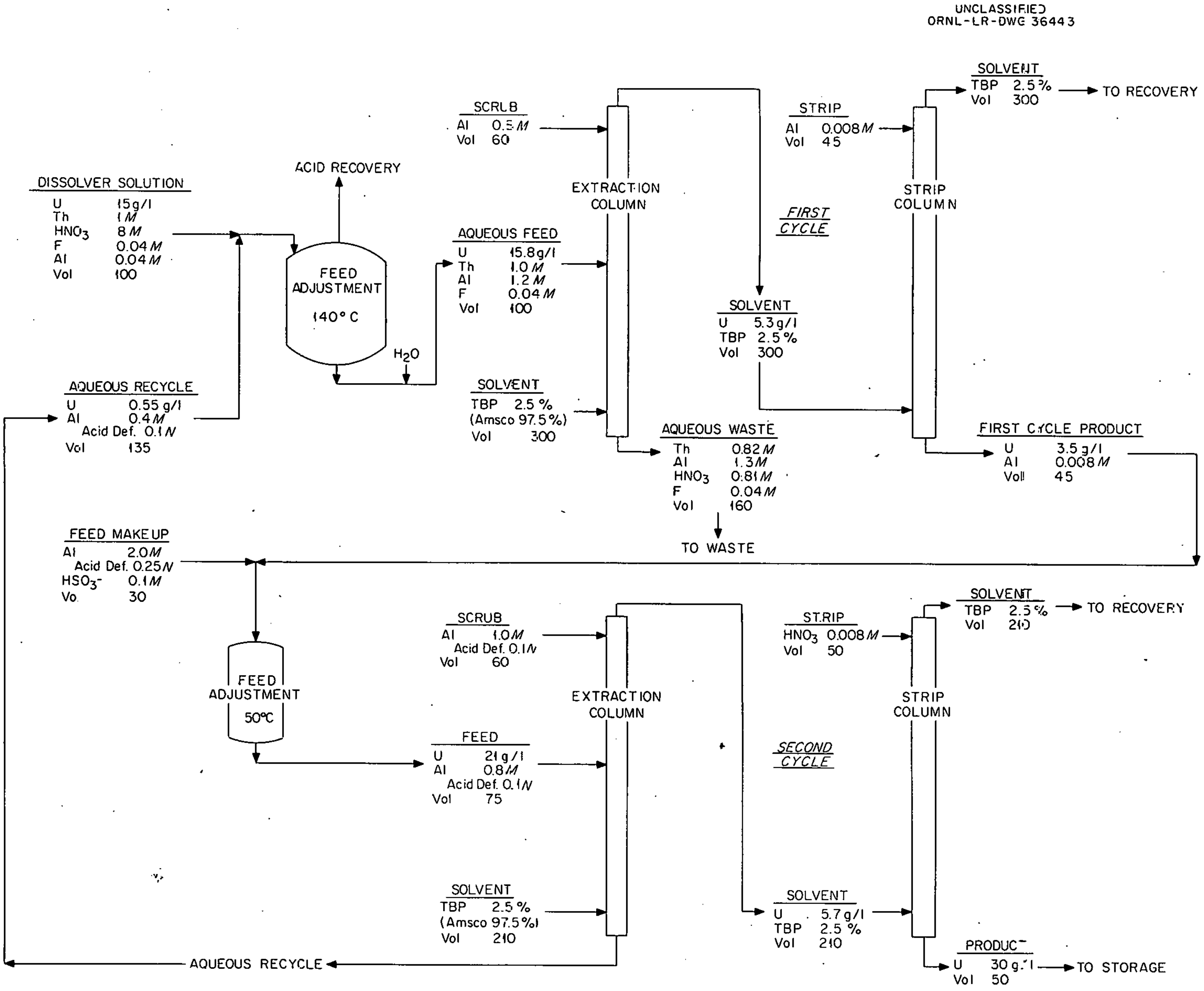

Fig. 23. Solvent Extraction Flowsheet for Consolidated Edison Fuel.

similar to those described above, showed first cycle decontamination factors for gross γ, Ru γ, Zr-Nb γ, and total rare earth β of 5×10^5, 4×10^4, 1×10^5, and 2×10^6, respectively. Second cycle decontamination factors were 8×10^4, 3×10^4, 6×10^4, and 1.5×10^5, respectively. The decontamination factors for the 2 cycles are not directly additive, however, since fresh fission product solution was used in each case.

Adaptation of the Redox Process to Stainless Steel Fuel Processing

Introduction - A series of preliminary studies were recently carried out jointly by members of Hanford Laboratory and Oak Ridge National Laboratory(21)(22). The purpose of these studies was to determine the feasibility of using the Redox flowsheet (involving the extraction of uranium and plutonium from fission products with methyl isobutyl ketone) for the recovery of the uranium and plutonium from spent stainless steel clad power reactor fuels. A limited number of both cold and hot solvent extraction experiments were carried out to determine the capacity of packed columns to measure decontamination factors, and to determine uranium losses. These scouting studies were performed at ORNL, and the results indicated that several modifications will be required in the basic Redox flowsheet in order to obtain reasonable decontamination factors for the first cycle solvent extraction process and at the same time minimize uranium losses.

Hot Experiments - The hot experiments were carried out in the Interim-23 solvent extraction facility in Bldg. 3503 at ORNL. This facility is shown schematically in Figure 24. The radioactivity during the hot experiments was provided by dissolution of natural uranium slugs from the graphite reactor. The dissolver product was adjusted in the feed adjustment tank by addition of iron, chromium, and nickel nitrate salts to prepare a simulated stainless steel power reactor fuel dissolution product. Constant lengths of 17 feet for extraction and 21 feet for scrubbing were used in the first column. The strip column was operated with 22 feet of effective length.

The results of these scouting studies are shown in Table 3. Run 1a was a standard Redox flowsheet. The overall decontamination factor of approximately 2,000 with a 0.03% uranium loss were the expected values for the experimental equipment. In Run 2, a slightly modified flowsheet was employed without radioactivity in order to measure the effect of a lower solvent flow ratio and the absence of an intermediate scrub stream added to the feed stream. A slightly higher uranium loss resulted from these changes.

The series of runs 3a through 3f was made with a feed which would be produced by the use of a Darex head-end treatment for stainless steel fuel

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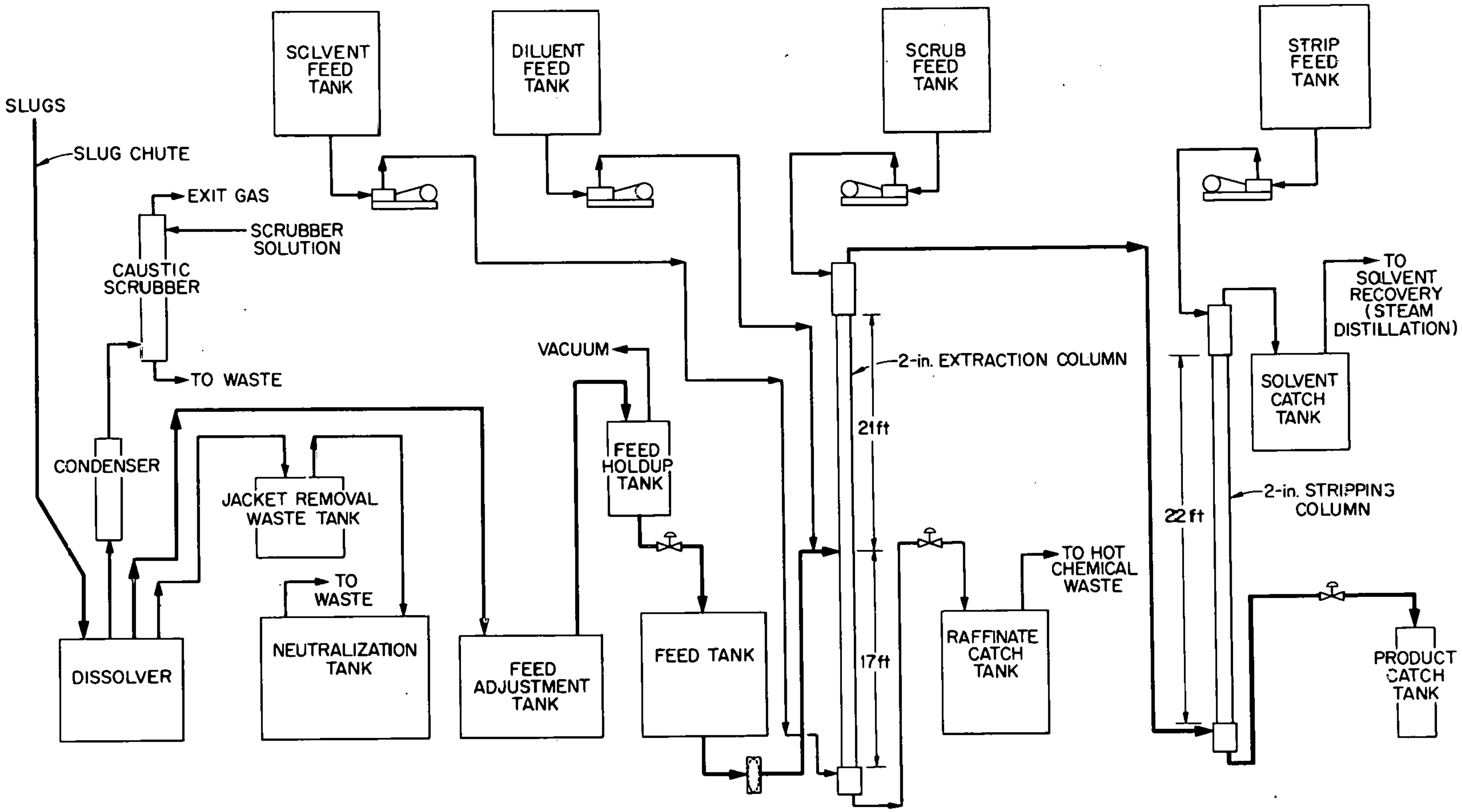

Fig. 24. "Interim 23" Solvent Extraction Facility - ORNL Bldg. 3503.

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TABLE 3.
SUMMARY
PILOT PLANT REDOX-TYPE RUNS

RUN NO.	SCRUB[a] FLOW RATIO	SOLVENT FLOW RATIO	SALTING STRENGTH (M)	H^+		U LOSS (%)	DF (GROSS γ)
				FEED (M)	SCRUB (M)		
1a	0.23[b]	3.50	1.19	-0.2	0.2[b]	0.0322	1,802
2	0.21	1.84	1.23	-0.2	0.2	0.0471	—
3a	0.31	2.44	1.38	-0.3	0.2	0.0019	59
3b-2	0.49	2.54	1.37	-0.3	0.2	0.0004	35
3c	0.53	2.66	1.36	0.5	0.2	0.0040	24
3e	0.28	1.49	1.10	-0.3	-0.15	0.1886	221
3f	0.76	1.95	1.08	0.05	-0.15	0.0097	283
8f	0.34	1.68	0.75	0.3	-0.15	0.0010	27
8g	0.51	1.80	0.78	0.2	-0.15	0.0089	53
8h-2	0.17	1.67	0.56	0.2	-0.12	0.1622	135

[a] RELATIVE TO FEED FLOW RATE OF 1.

[b] USED ALSO "INTERMEDIATE SCRUB," FLOW RATIO = 0.53, H^+ = -0.2 M, Al = 2.5 M, U = 0.045 M.

FEED: 1.9 - 0.2 M U
1.2 - 0.0 M SS
1.6 - 0.0 M Al
$2.2 \times 10^8 - 5.5 \times 10^7$ cts/min·ml GROSS γ

SCRUB: 1.3 - 1.0 M Al

elements. A typical feed was approximately 0.6 molar uranium, 1.2 molar stainless steel, and from 0.3 acid deficient to 0.5 acid. The results of these runs indicated that a low salting strength was required for adequate decontamination but a higher solvent ratio must be maintained in order to avoid excessive uranium losses. Even with these modifications the overall decontamination factor was lower by a factor of 6 than in the case of the standard Redox flowsheet.

Runs 8f, g, and h-2 were made with a feed which would be typical of that produced by the Niflex head-end treatment. A typical feed stream would contain 0.3 molar uranium, 0.8 molar aluminum, 0.3 molar acid, 0.2 molar stainless steel, and 0.8 molar ammonium fluoride. Due to the complexing of the aluminum by the fluoride ions a lower effective salting strength was used during the three Niflex runs and the feed was maintained acid at all times to prevent precipitation within the column.

As the salting strength was reduced, the uranium losses increased much more rapidly than the decontamination factor increased. The maximum decontamination factor obtained in the Niflex runs was a factor of 13 below the decontamination factor of the standard Redox run. Obviously the Redox flowsheet must be modified substantially if it is to be used for the recovery of uranium from stainless steel fuels which have had a Niflex head-end treatment.

Cold Experiments - The cold runs were carried out in an experimental packed column shown in Figure 25. The results of the cold runs are summarized in Table 4. Run 1 was a standard Redox flowsheet while runs 3a through 3h were Redox flowsheets with a Darex head-end treatment. Run 8 was a Redox flowsheet with a Niflex head-end. The feed compositions used during the cold runs were approximately the same as those in the pilot plant hot runs with the exception that no fission product activity was present.

The purpose of the cold runs was to determine the extraction column capacity or flooding rate and to measure uranium losses under conditions such that HETS might be calculated. Based upon the cold runs all pilot plant hot runs were carried out at approximately 80% of the total flooding rates. Runs 3a, 3h, and 8 were made for the purpose of determining flooding rates only and no uranium loss or HETS was calculated. So long as the feed

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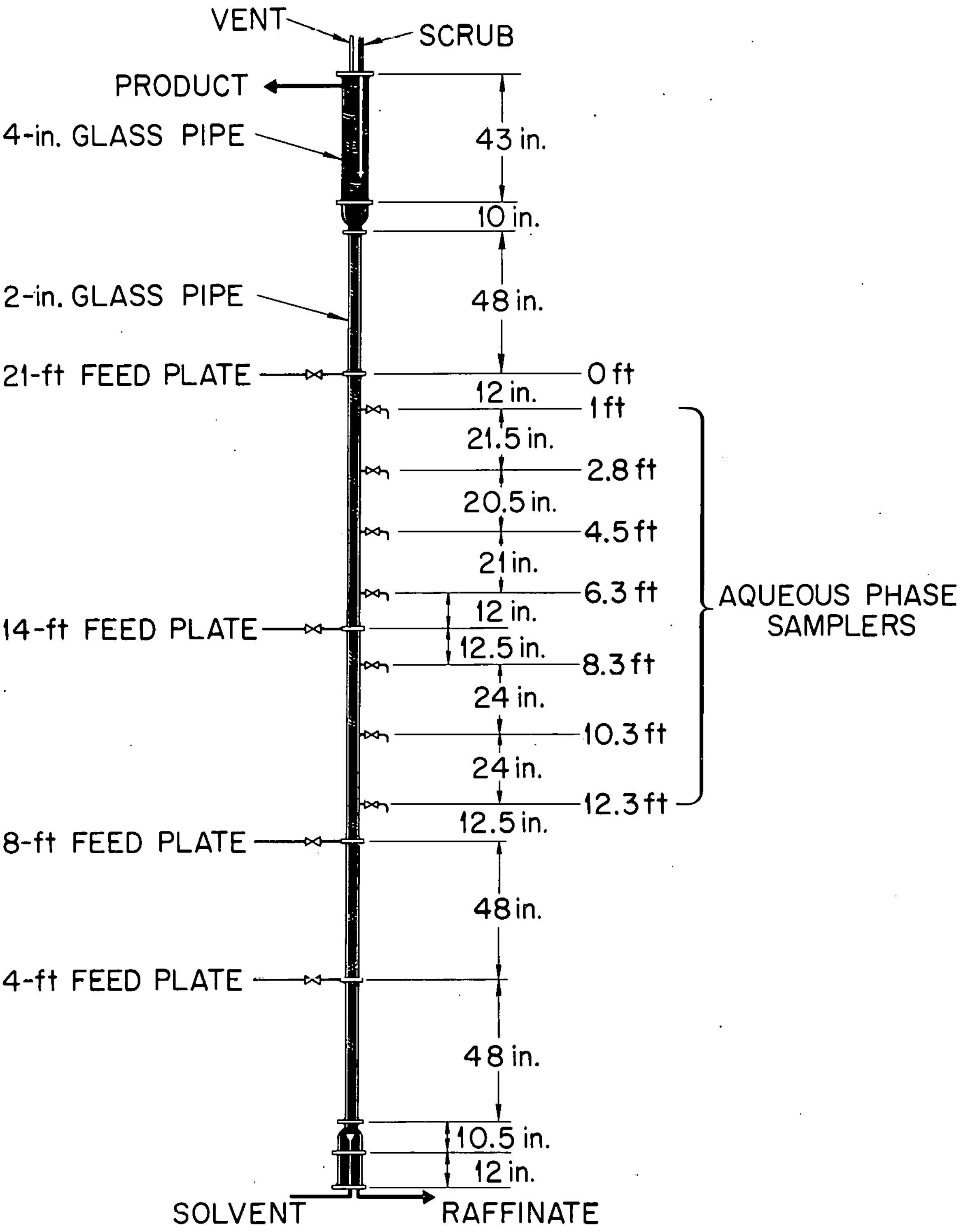

Fig. 25. Experimental Packed Column for Non-Radioactive Tests - ORNL Bldg. 3503.

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TABLE 4
SUMMARY
UNIT OPERATIONS REDOX-TYPE RUNS

RUN NO.	SCRUB[a] FLOW RATIO	SOLVENT[a] FLOW RATIO	SALTING STRENGTH (M)	H^+ FEED (M)	H^+ SCRUB (M)	Si (ppm)	FLOODING RATE (GSFH)	U LOSS (%)	HETS (ft)
1	0.15	2.3	1.23	-0.3	0.2	—	589	0.00168	2.0
3a	0.25	2.0	1.50	-0.2	0.2	15	>640	—	—
3b	0.5	2.5	1.47	-0.2	0.2	15	557	0.00175	3.6
3e	0.3	2.1	1.10	-0.3	-0.1	308	333	0.00272	1.4
3h	0.24	2.5	0.99	-0.25	-0.2	448	295	—	—
8	0.2	1.85	0.64	0.3	-0.1	28	664	—	—

[a] RELATIVE TO FEED FLOW RATE OF 1.

FEED: 1.2 - 0.4 M U
1.3 - 0.0 M Al
1.4 - 0.0 M SS

SCRUB: 1.3 - 1.0 M Al

acidity was increased to compensate for the decreased solubility of the components of the feed (compare runs 3a and 8) approximately the same flooding rates were obtained for Darex and Niflex feed. The most important variable affecting flooding rate was the silicon content of the feed. As the silicon content was increased in the case of Darex runs the flooding rate decreased steadily. The rate was reduced by more than a factor of 2 as the silicon content increased from 15 to 448 ppm.

In all cases the uranium losses were extremely low and HETS values ranged from 1.4 to 3.6 with no significant effect of the Darex head-end treatment on the HETS values. Data for the pilot plant Run 3e were analyzed to determine HETS and a value of 1.2 feet was caluclated, comparing closely with the value obtained for cold Run 3e.

The calculation of the HETS value for Run 1 is illustrated in Figure 26. Under the flowsheet conditions an extremely flat scrub operating line was used. Thus there was essentially no uranium refluxing to the feed point from the top portion of the column. Conditions at the bottom of the column (as shown by the lower end of the operating line) were determined by a small amount of uranium contained in the fresh solvent feed stream and the uranium losses in the raffinate. Since the column contains several aqueous sample points it was possible to compare HETS values for several regions of the column. The HETS value calculated for the top 6.3 feet was approximately 2 feet for Run 1, indicating that there was no significant effect of aqueous phase concentration on the values of HETS.

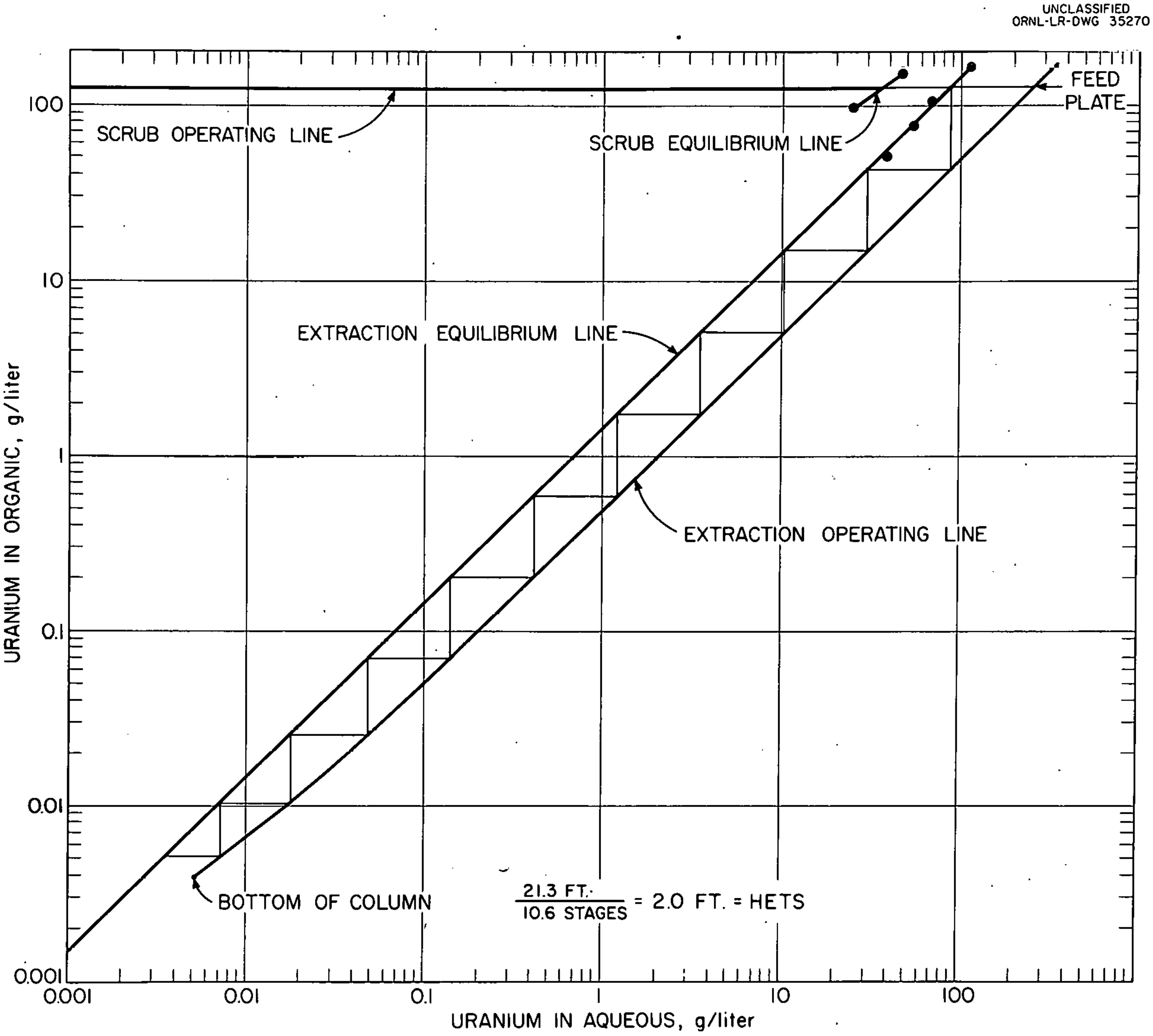

Fig. 26. HETS Calculation for Run 1. Redox solvent extraction in 2-in. glass packed column.

New Solvents for Power Reactor Fuel Reprocessing

The possibility of using solvents other than tributyl phosphate for the reprocessing of spent power reactor fuels is being investigated. This search is being conducted with the hope of finding solvents that might offer one or more of the following advantages over tributyl phosphate:

1. Increased capacity for uranium or thorium extraction, permitting higher plant throughputs for fixed equipment sizes.

2. Enhanced separation of source and fissionable material from fission products and from each other, permitting fewer solvent extraction cycles.

3. Increased radiation and chemical stability, permitting operation with higher specific fission product activity solutions, and the simpler solvent regeneration procedures.

4. Metal extraction from systems that are not amenable to tributyl phosphate processing, making possible the recovery of uranium and plutonium from sulfuric acid- and fluoride-containing dejacketing solutions.

5. Replacement of ion exchange in the final product isolation and purification steps with concomitant simplification of operations.

6. Recovery of by-products such as fission products, neptunium, and transplutonics, which may in the future constitute a source of revenue for the fuel reprocessor.

The search for new solvents at the Oak Ridge National Laboratory centers around those reagents which have been used with outstanding success in the recovery of uranium and thorium from their ores.(23,24) In general, the solvents fall into two categories, organophosphorus compounds and amines. The organophosphorus compounds(25) may be further subdivided into acid extractants and neutral extractants. The acid extractants include the mono- and dialkyl phosphoric acids. These reagents extract metals by a cation exchange reaction involving replacement of the acidic hydrogen of the reagent with the extracted metal ion. The neutral extractants include the trialkyl phosphates, phosphonates, phosphinates, phosphine oxides and dialkyl phenyl phosphonates. These reagents extract neutral complexes.

Basic extractants, the amines,(26) fall into the following categories: primary, secondary, and tertiary. In addition, strong-base quaternary compounds capable of extracting metals at high pH's are being studied. The extraction behavior of the basic reagents is similar to sorption by the amine or alkyl ammonium groups in anion exchangers.

Extraction of Metals by Alternative Solvents. Table 5 shows typical extractions by the new reagents of metals of interest to power reactor fuel reprocessing. Thorium, uranium, neptunium, tri- and tetravalent plutonium, and americium are only slightly extracted by primary and secondary amines from dilute nitric acid. The tertiary amines and quaternary ammonium compounds extract the tetravalent ions, while only the phosphine oxides extract the trivalent plutonium and americium.

The extraction of most of these metals by the reagents shown increases with increasing nitric acid concentration up to about 8 M. If the nitrate ion in the system is replaced with sulfate or phosphate, the extraction by the acidic and neutral reagents is found to be much lower than from nitric acid. The amine extraction behavior, however, is completely inverted, with the extraction of the tetravalent ions from sulfate solutions being high in the case of the primary, and low in the case of the tertiary amines. The extraction relation may be modified considerably by changing the extraction conditions and by altering the reagent structure. The case of uranium-thorium extraction is a good example of how reagent behavior may be altered by changing structure.

Alternative Solvents for the Separation of Uranium and Thorium. Several solvents were investigated as alternatives to tributyl phosphate for uranium and thorium extraction in the Thorex process. Table 6 presents the ratio of the uranium to thorium distribution coefficients or separation factors as a function of nitric acid concentration. The phosphate esters are arranged in order of increasingly close branching to the central phosphorus atom and of increasing length of the branched chains. In this series of solvents the selectivity of uranium increases slightly through the first four reagent structures and then increases by an order of magnitude on the introduction of secondary alkyl groups. The uranium extraction with tri-sec-butyl phosphate is approximately the same as with the preceding reagents, and the increased separation factor results from much lower thorium extraction.

Table 5. Typical Extractions from Nitric Acid
($2\ \underline{M}\ HNO_3$, $\sim 0.3\ \underline{M}$ extractant)

Metal	E_a^o						
	RNH_2	R_2NH	R_3N	R_4N^+	R_3PO	R_2HPO_4	R_2HPO_4 + R_3PO
Th(IV)	<0.01	<0.1	~ 1	50	> 1000	> 1000	> 1000
U(VI)	<0.01	<0.1	0.5	2	> 1000	500	> 1000
Np(IV)		0.1	50	200	> 200	> 1000	
Pu(III)	<0.01	<0.1	<0.1	< 1	~ 10	< 1	
Pu(IV)	0.02	0.5	500	50	> 1000	> 1000	> 1000
Am(III)	<0.01		0.2		1	< 0.01	0.05

Table 6. Reagents for Uranium-Thorium Processing

Extractant (1 $\underline{M}$)	Separation Factor (E_a^o (U)/E_a^o (Th))			
	2 $\underline{M}$ HNO_3	4 $\underline{M}$ HNO_3	6 $\underline{M}$ HNO_3	10 $\underline{M}$ HNO_3
Tributyl phosphate	15	15	15	5
Triisobutyl phosphate	20	20	20	10
Tri(2-methylbutyl) phosphate	10	15	20	15
Tri(2-ethylhexyl) phosphate	30	25	30	20
Tri-<u>sec</u>-butyl phosphate	200	250	220	90
Dibutyl butyl phosphonate	10	15	7	2

Uranium extraction by dibutyl butyl phosphonates is an order of magnitude higher than with the phosphates, but thorium extraction increases even more, with a resulting slight decrease in the separation factor.

Plutonium Extraction. The amine solvents appear very promising for the extraction of plutonium from nitrate and sulfate systems. Figure 27 shows tetravalent plutonium distribution coefficients as a function of nitric acid concentration. Tertiary amines show higher extraction than the quaternary at 1 and 2 M nitric acid; however, with increasing acidity, the extraction power of the quaternary amines overtakes that of the tertiary, and the quaternary is much more effective at an acid concentration of 8 M. Figure 28 shows the effect of amine concentration on the tetravalent plutonium distribution coefficient. In each case the measurements were made at the nitric acid concentration that gave the maximum extraction for each solvent type. In the case of the quaternary amine the slope of the extraction isotherm is a little less than 1, a little less than 2 for the primary amine, and between 3 and 4 for the tertiary amine. Although such slopes usually indicate ligand numbers in the extracted complex, this does not apply in the case of uranyl sulfate extraction by amines, so no attempt is made here to infer ligand numbers.

A number of reagents have been studied for the extraction of plutonium from solutions of Purex composition and from diluted Sulfex decladding solutions. The results are shown in Table 7. In this series of compounds

Table 7. Plutonium Extraction from Nitric and Sulfuric Acid Solutions

Extractant	Conc., M	E_a^o (Pu(IV))	
		2 M HNO_3	3 M H_2SO_4
Tri-n-octyl phosphine oxide	0.3	1500	30
Di(2-ethyl hexyl) phosphoric acid	0.4	5000	4
Di(2-ethyl hexyl) phosphoric + tri-n-octyl phosphine oxide	0.4 0.1	10,000	2
Primene JM-T	0.3	0.02	> 1000
Amine S-24	0.3	0.4	< 1
Tri-n-isooctyl amine	0.3	500	< 0.1
Quaternary B-104	0.1	20	
N-Benzylheptadecyl amine	0.1		6

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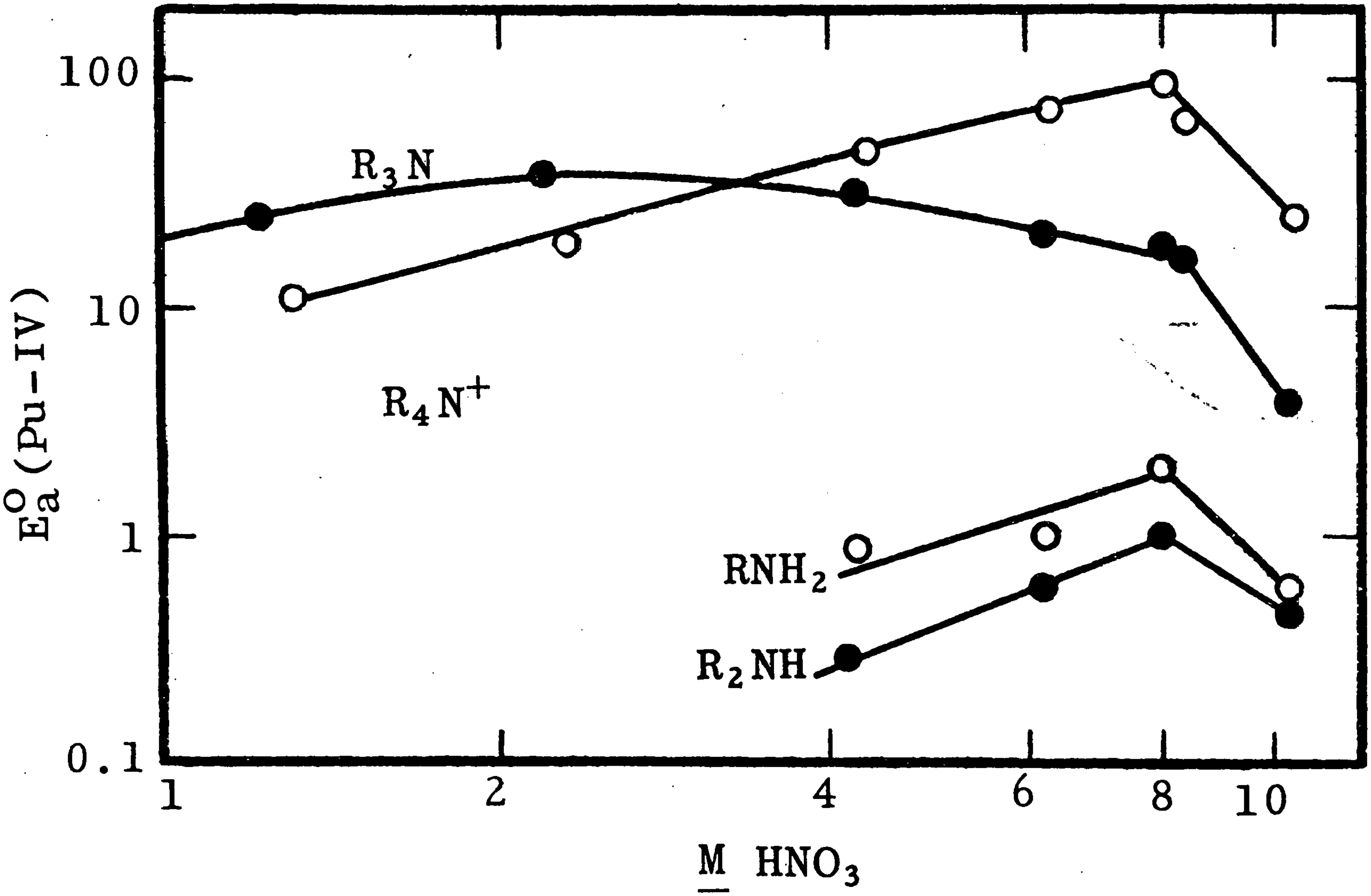

Fig. 27. Pu(IV) Extraction by 0.1 M Amine vs HNO_3 Concentration.

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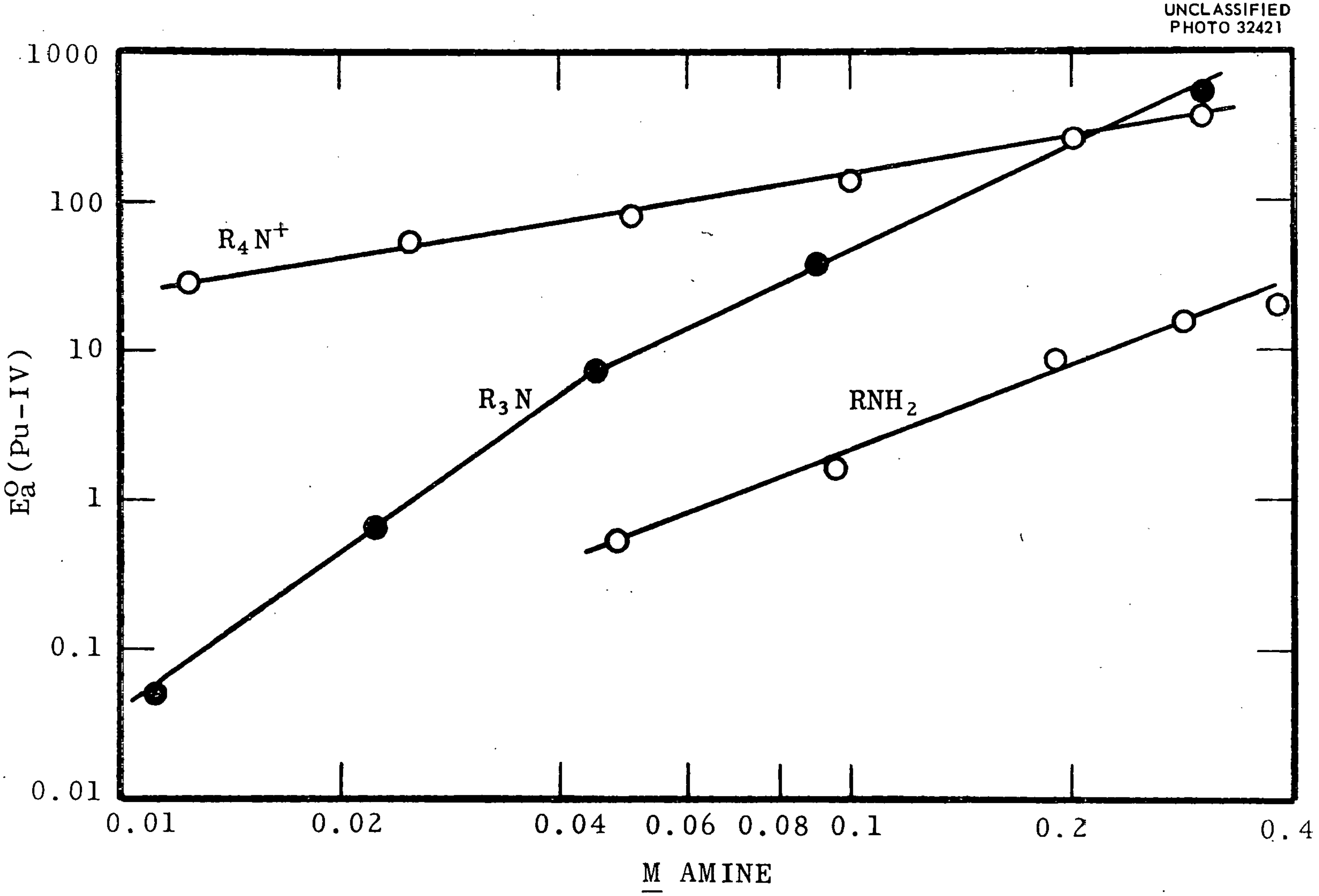

Fig. 28. Pu(IV) Nitrate Extraction vs Reagent Concentration.

the first two extractants are phosphorus reagents, tri-n-octyl phosphine oxide and di-2-ethyl hexyl phosphoric acid, and the third is a synergistic mixture of the first two. The others are amines: highly branched primary and secondary, moderately branched tertiary and quaternary, and N-benzyl secondary amine. These data show the marked effect of aqueous sulfate complexing on extraction by the acidic and neutral reagents and also the inversion between nitrate and sulfate media in extractions by the different classes of amines. Neutralization of the sulfuric acid would increase extraction by the amines but would impair extraction by the dialkyl phosphoric acid slightly and by the phosphine oxide severely.

The primary amine Primene JM-T strongly extracts tetravalent uranium, as well as plutonium, from sulfuric acid solution. This has suggested its use for the recovery of plutonium and uranium from Sulfex decladding solutions. A flowsheet for the amine extraction of uranium and plutonium from Sulfex decladding solutions is shown in Figure 29. After extraction from the sulfate solution the plutonium and uranium would be stripped with dilute nitric acid, or with sodium carbonate and then acidified with nitric acid, and returned to a nitrate extraction system. The amine nitrate would be regenerated to the free-base amine for recycle. Neither ferric nor ferrous iron is extracted significantly. This process is to be installed in the Oak Ridge Power Reactor Fuel Reprocessing Pilot Plant.

Radiation Damage to Solvents. Tributyl phosphate is partially decomposed by radiation to dibutyl phosphoric acid which forms solvent-soluble compounds with uranium, plutonium, zirconium, and niobium, but which forms a very insoluble compound with thorium. Formation of solvent-soluble compounds is noticeable at 0.05 watt-hr/liter dose density, but precipitation of thorium dibutyl phosphate requires about 0.4 watt-hr/liter. These doses cause decomposition of about 0.002 and 0.016% of the TBP in a 40% Amsco solution, respectively,(27) and would complicate solvent repurification operations. Deleterious effects on TBP limit the tolerable radiation doses in the first cycle extraction column to about 0.4 watt-hr/liter in the Thorex process, and to about 1 to 2 watt-hr/liter in the Purex process. These values, in turn, would define the minimum fuel decay time and the associated

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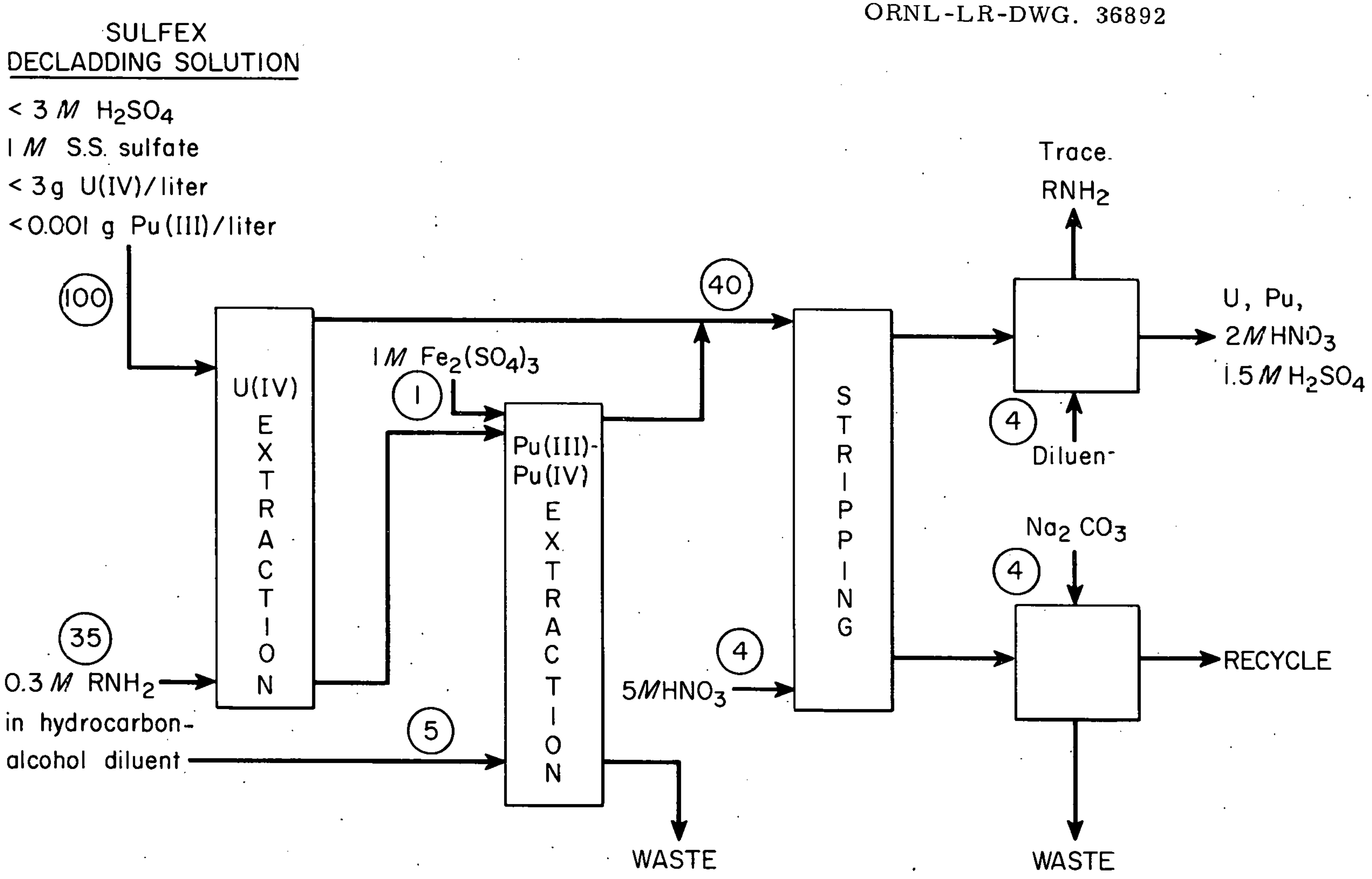

Fig. 29. Amine Solvent Extraction Recovery of Uranium and Plutonium from Sulfex Decladding Solution.

fissile inventory charges. Studies are being conducted to find extractants that are less deleteriously affected by radiation because of either (1) greater stability toward radiation decomposition or (2) formation of radiolysis products that do not form soluble or insoluble compounds with the fissile, fertile, or fission product elements.

With the exception of dibutyl phenyl phosphonate and dibutyl butyl phosphonate, with G values for radiolytic decomposition of about 0.78 and 1.5 molecules/100 ev, respectively, all extractants tested to date are affected to about the same extent as TBP; i.e., the G value for decomposition is between 2 and 4 molecules/100 ev.

Five amines (Table 8) have been irradiated to the 200 or 400 watt-hr/liter level and, along with unirradiated samples, have been subsequently used in uranium--fission product extraction and decontamination tests. These irradiation levels are 400 to 800 times higher than the highest yet encountered in radiochemical reprocessing operations. Uranium distribution coefficients were essentially unchanged by the radiation exposure; decontaminations of uranium from fission products by trilaurylamine and Alamine 336 were not increased by the radiation exposure; however, under the conditions used, decontaminations by Primene JM-T, N-benzyl heptadecyl amine, and tri-isooctyl amine were decreased by factors up to 11 in the extraction step.(28)

Table 8. Radiolysis Yields and Fission Product Extraction

Amine	Radiation Dose, watt-hr/liter	Target Decomposition, molecules/100 ev	Fission Product Extraction,[a] Irradiated/Control	
			Gross γ	Gross β
Primene JM-T	400	2.25	1	3.4
N-benzyl heptadecyl amine	200	2.14	7.5	8.7
Tri-isooctyl amine	400	---	11	10
Alamine 336	400	3.49	1.5	0.1
Trilauryl amine	400	---	0.13	0.86

[a] 0.1 M amine in xylene as organic phase, 0.2 M uranyl nitrate plus fission products in 8 M HNO_3 aqueous phase.

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