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PUREX PROCESS OPERATION AND PERFORMANCE 1970 THORIA CAMPAIGN

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Research and Engineering Process Engineering

February 1978

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To be presented at:

AICHE 84th National Meeting
Atlanta Ga.

February 26 through March 1, 1978

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PUREX PROCESS OPERATION AND PERFORMANCE:
1970 THORIA CAMPAIGN

ABSTRACT

The Hanford Purex Plant has demonstrated suitability for reprocessing irradiated thoria (ThO_2) target elements on a campaign basis. A 1965 process test and major production campaigns conducted in 1966 and 1970 recovered nitrate solution form products totaling approximately 565 tons of thorium and 820 kilograms of ^{233}U . The overall recoveries for the 1970 campaign based on reactor input data were 94.9 percent for thorium and 95.2 percent for uranium.

The primary function of the Hanford Purex Plant is reprocessing of irradiated uranium fuel elements to separate and purify uranium, plutonium and neptunium. Converting the plant to thoria reprocessing required major process development work and equipment modifications. The operation and performance of the Plant during the 1970 thoria reprocessing campaign is discussed in this report. The discussion includes background information on the process and equipment, problems encountered, and changes recommended for future campaigns.

PUREX PROCESS OPERATION AND PERFORMANCE: 1970 THORIA CAMPAIGN

INTRODUCTION

The primary function of the Hanford Purex Plant is the aqueous reprocessing of irradiated uranium metal fuel elements for the separation and purification of uranium, plutonium and neptunium. However, a number of programs implemented since plant startup in January 1956 have provided capability for reprocessing a variety of materials, including irradiated thoria (ThO_2) target elements, on a campaign basis.

The first Purex production scale thoria campaign conducted in 1966 resulted in the recovery of approximately 165 tons of thorium and 220 kilograms of ^{233}U as nitrate solutions. The 1970 thoria campaign resulted in the recovery of approximately 400 tons of thorium and 600 kgs of ^{233}U . The preparation, operation and performance of the Purex Plant during the second or 1970 thoria reprocessing campaign are discussed in this presentation, which is based on ARH-2127, R. R. Jackson and R. L. Walser, March 1977, "Purex Process Operation and Performance: 1970 Thoria Campaign."

PLANT PREPARATIONS

Preparation of the Purex Plant for the Thorium Run consisted of six major parts:

1. Pre-Shutdown Activities;
2. Plant Shutdown;
3. Product Recovery Flushes;
4. Equipment Change-Out;
5. Final Decontamination Flushes; and
6. Plant Operability Testing.

Pre-Shutdown Activities

Plant preparation for the 1970 thoria campaign began in mid-December 1969 as a purge of uranium (^{238}U) from the Purex recovered acid system was started. The purge was accomplished by routing nitric acid recovered at the Uranium Oxide (UO_3) Plant, the source of uranium, directly to the dissolvers rather than into the Purex recovered acid system. Procedural controls were imposed to assure the UO_3 acid always met dissolver specifications. As the Purex acid inventory turned over, the uranium content dropped from a normal of 200-500 pounds to less than 20 grams at shutdown in June 1970.

Other pre-shutdown activities included flushing the alternate plutonium concentration equipment in preparation for isolation and preparing the waste rework tank to receive the concentrated backcycle waste inventory and product flushes following shutdown.

Plant Shutdown

At shutdown, the plutonium and neptunium inventory in process was reduced to a minimum by processing recycled uranium nitrate solution. The recycle operation permitted extensive heel dissolution for removal of most of the uranium, plutonium, and neptunium from the dissolvers and head end (feed preparation and storage) tanks. The heel removal solutions were then blended and processed with recycled uranium. As processing of the recycled uranium began, a decontamination and concentration sequence was started in the Second Neptunium Cycle to remove the maximum amount of neptunium from the backcycle waste system. Also, as fission product activity decreased during processing of recycle feed solution, the second cycle extraction columns were operated with negligible losses.

Product Recovery Flushes

Extensive plant flushing was required as the allowed ^{238}U content in the ^{233}U product of 0.5 weight percent was equivalent to only 6.6 pounds of ^{238}U for the entire campaign. Three 1,000 gallon water flushes of the high-level waste system were made to the boiling waste interim storage tank. The system was then flushed with five percent caustic - two percent sodium tartrate and with water to non-boiling waste. These flushes prepared the high-level waste system for concentration of product removal flushes.

The product removal flushes consisted of repeated dilute nitric acid flushes of head end vessels and individual solvent extraction cycles until the product values were low. The flushes were boiled down in the high-level waste (1WW) concentrator to permit partial recovery of the nitric acid boiled off in the acid absorber. The concentrated waste was transferred to the waste rework tank for storage and was followed by low volume water flushes.

Equipment Changeout

Extensive equipment modifications, including approximately 275 remote piping jumper changes, were required to changeover to thorium processing. Major equipment changes made for the campaign included the installation of two new concentrators (feed concentration-denitration and first cycle uranium product), a new downdraft condenser tower on the TK-A3 dissolver, and a new uranium product receiver tank. Numerous new instruments and changes in the range or alarm set point of previously installed instruments were required to accommodate the revised flow conditions and to provide additional monitoring.

Final Decontamination and Cleanup Flushes

The final removal of uranium from the head end vessels was accomplished with potassium fluoride-aluminum nitrate in concentrated nitric acid. The flush approximated the starting chemical conditions of thoria dissolution. Vigorous sparging and long-time exposure were essential.

The strong nitric acid-fluoride flushes used in the dissolvers were also used to flush out the feed system tanks (Tanks D3, D4, D5, E6 and H1) and the coating waste treatment system (Tanks D2 and E3, the centrifuges G-E2 and G-E4).

The solvent extraction cycles were flushed individually using a sequence of flushes consisting of a five percent oxalic acid - three percent nitric acid solution, followed by a water flush, then a five percent caustic - two percent sodium tartrate solution, followed by a water flush. The acidic flushes and initial water flushes were all accumulated and processed before starting the caustic flushes. Samples of the individual flushes indicated that the back cycle waste tank (TK-J1) and the neptunium cycle feed tank (TK-J21) required additional flushing. The uranium was attributed to siliceous solids known to accumulate in these tanks. A special metathesis-type flush which consisted of digesting a sodium hydroxide-sodium carbonate solution in each tank, was used. Then, after jetting out the basic solution, a dilute nitric acid solution was added to dissolve the soluble compounds formed by the metathesis solution. The same solution was routed through TK-F12. This flush removed 1WW solids which accumulated when TK-F12 was previously used for 1WW rework storage. A total of 360,000 gallons of waste was routed to underground storage tanks during these operations.

The N Cell equipment was flushed solely with nitric acid. The N Cell flushing was discontinued after the plutonium level dropped to less than 0.1 gram in a flush. These flushes were concentrated with the above acidic and water flushes of the solvent extraction system.

Operability Testing

After the completion of chemical flushing and equipment/piping changes, the process equipment was operability tested. This shakedown run consisted of recalibrating all flow measurement devices, operating all equipment at thorium rates, and conducting a sampling program designed to ascertain the remaining ^{238}U levels.

Most of the problems encountered were easily solved. However, a new vent jumper was required to enable maintaining adequate vacuum in the TK-A3 dissolver. Repairing leaks and correcting a number of mistakes in the 1BXT jumper was required before marginal flowrates could be maintained.

Throughout the operability test, the ^{238}U levels in the process samples were acceptably low.

FLWSHEET

The 1970 thoria campaign flowsheet was essentially the same as that used for the 1966 thoria campaign.

Target Decladding (Slide #2) and Dissolution (Slide #3)

The aluminum cans containing the thorium powder (325 mesh to 6 mesh particles vibratory compacted to a bulk density of 7.5 grams per cubic centimeter) or wafers (cold pressed and sintered to right cylinders 1.5 inches in diameter by 2.8 inches long with a bulk density of 7.6 g/cc) were dissolved by the conventional sodium nitrate sodium hydroxide process. During decladding, the off gas was scrubbed with water to remove ammonia for disposal to an underground trench, then passed through a steam heater, electric heater, silver reactor, and two fiberglass filters to the stack.

The thorium targets (approximately 3.2 tons ThO_2 per charge) were dumped into sufficient 1.9 M NaNO_3 to cover the charge, and the dissolver contents were heated to boiling. Sufficient 19.0 M caustic was added at a controlled rate to achieve a caustic-to-aluminum mole ratio of 2.25. The dissolver contents were digested at boiling temperature for two hours to complete the aluminum-cladding removal. The decladding solution was then cooled and jetted to the decladding waste treatment system where the solution was centrifuged to recover any thorium particles entrained from the dissolvers. The resulting thorium cake was washed with 8 M caustic and then with water. The cake was slurried from the centrifuge to a digest tank with four batches of concentrated nitric acid. The resulting slurry was butted with fluoride (KF) which was complexed with aluminum nitrate. A six-hour digest at 70°C proved adequate to dissolve the thorium. The decladding solution which passed through the centrifuge and the cake washes were discarded to a non-boiling waste underground storage tank.

After aluminum de-jacketing, the thoria, as powder or wafers, was dissolved with a nitric acid-potassium fluoride-aluminum nitrate solution. The potassium fluoride was added in two increments; the first at the beginning of the dissolution, the second after two hours of digestion. The aluminum nitrate used to complex the fluoride was also added in two increments; the first prior to starting the dissolution, the second at completion of the dissolution. After digestion at boiling temperature for 16 to 18 hours for powder or 10 to 12 hours for wafers, the dissolver contents were cooled and jetted to lag storage tanks prior to concentration to meet feed requirements.

During the dissolution operation, the off gas followed the route described above for decladding except no water was added to the ammonia scrubber tower and the stream, after leaving the filters, was also routed through the two acid absorber columns located in the Purex BaCkup Facility. A continuous monitor normally used to detect iodine in the dissolver off gas-stream was adjusted to permit detection of ruthenium.

The absorber columns were operated on reflux water alone during the thoria campaign due to the low nitric acid content of the off-gas. Operation in this manner resulted in some ruthenium decontamination as evidenced by analyses of reflux water samples. Fresh demineralized water additions were made when the tank contents were changed out or to replace evaporation losses.

Feed Concentration and Denitration (Slide #3)

The cake dissolution and dissolver solutions were then combined for concentration and distillation to produce an acid-deficient thorium nitrate solution as feed for the first solvent extraction cycle. In the concentrator, the thorium concentration of the blended solution was increased from the initial value of 0.5 to 0.7 M to a final value of 3.0 M with a corresponding volume reduction from the initial 15,000 to 11,000 gallons of 2,500 gallons. Water

was then continuously added to the concentrator while boiling at a constant volume to remove nitric acid to a 0.2 M acid deficient end point. The concentrated solution was then transferred while still at a temperature of about 75°C (well above the 55°C freezing point of the solution) to the receiver tank (TK-F10) with a submerged jet which used demineralized water as the motive force. The water also provided the required dilution. Finally, the feed was adjusted to the desired 1.5 M thorium and -0.10 M nitric acid concentrations.

The concentrator off-gas stream passed through a demister pad and a condenser to the vessel vent system. The demister pad reduced the radionuclide content of the off-gas and aluminum nitrate was added via the upper spray nozzle to complex any free fluoride on the pad. The condenser condensate was routed to the Acid Recovery System. An alternate route to the second cycle waste receiver tank (TK-F10), provided for use if the radionuclide content became unacceptably high, was not used.

Solvent Extraction

The solvent extraction flowsheet was based on the Thorex II process developed at the Oak Ridge National Laboratory and development work conducted at other sites. The first solvent extraction cycle was used for co-decontamination and partitioning of the thorium and the ²³³U. Further decontamination of the products was attained in one additional thorium and two additional uranium solvent extraction cycles. A solvent consisting of 30 volume percent tributyl phosphate diluted with normal paraffin hydrocarbons (n-C₁₀ to n-C₁₄) and pulse column contactors were used in all cycles. The Third Uranium Cycle aqueous product stream (3BU) was also passed through a fixed bed of cation resin for thorium absorption prior to final concentration.

Co-Decontamination and Partitioning Cycle (Slide 4)

The prepared aqueous feed (HAF) was pumped to the HA (T-H2) Column where the thorium and uranium were co-extracted into the organic phase (HAX) leaving most of the other radio-isotopes in the aqueous phase. The organic 1BSU recycle stream was also pumped from TK-J2 to the HA Column as the HAO. The organic was scrubbed in the top of the HA Column by the aqueous HAS stream. This dilute nitric acid solution also contained small amounts of phosphoric acid and ferrous sulfamate to improve the plutonium, chromium, protactinium and zirconium-niobium decontamination. A 13 M HNO_3 stream (HAX- HNO_3) from the recovered nitric acid header was added near the bottom of the column to control the thorium waste loss. The combined aqueous stream exited the bottom of the column as the HAW. The combined organic stream, bearing the thorium and uranium exited the top of the column as the HAP.

The 1BXF feed to the Partition Cycle was composed of the organic overflow from the HA Column (HAP) and the organic waste streams from the Second and Third Uranium Cycles (2BW and 3BW). The separation of thorium and uranium was accomplished by stripping (back-extracting) the thorium from the organic phase with 0.2 M HNO_3 .

The uranium-bearing organic stream (1BU) flowed by gravity to the bottom of the 1C Column (T-H3), where the uranium was stripped out of the organic with 0.01 M HNO_3 (1CX). The product-bearing aqueous stream (1CU) then exited the bottom of the 1C Column and was routed via a steam operated jet to the 1CU concentrator (E-H4), where it was concentrated to Second Uranium Cycle feed requirements.

The thorium-bearing aqueous stream (1BXT) was routed via an air-lift to the top of the 1BS Column (T-J7). Here, it was scrubbed with an organic stream (1BS) from the No. 1 Solvent header to re-extract any uranium which may have stripped out of the 1BX Column. The organic scrub (1BSU) was routed to TK-J2 and recycled to the HA Column as the HAO stream. The aqueous stream (1BT) was routed to the 1BT (E-J8) concentrator and boiled down to Final Thorium Cycle feed requirements.

Second Thorium Cycle (Slide 5)

The concentrated thorium stream from the Partition Cycle (1TC) overflowed the 1BT Concentrator (E-J8) to the 2DF feed tank (TK-K1). A stream containing ferrous sulfamate was also added to the feed to reduce any residual plutonium to the nearly inextractable plus three valence. The combined streams were pumped as the feed to the midpoint of the dual-purpose, extraction-scrub, 2D Column where the thorium was extracted into the 30 volume percent TBP-NPH solvent (2DX) while the plutonium and most of the remaining fission products exited via the aqueous 2DW waste stream. The 2DW stream was routed to TK-F10 in the Waste Concentration and Acid Recovery System for further processing and transfer to an underground waste storage tank.

An intermediate scrub stream (2DIS) containing concentrated nitric acid (12.2 M) and, originally, 0.66 M phosphoric acid was added by gravity flow from aqueous makeup tanks to an entry point midway between the feed and the top of the column. The primary purpose of the nitric acid was to provide additional salting strength in the column to prevent excessive thorium losses to the 2DW stream. The phosphoric acid was intended to increase the protactinium decontamination attained in the column. However, this constituent was eliminated during most of the run due to the low protactinium content of the feed and to precipitation

problems discussed later. A water scrub stream (2DS) was added to the top of the column by gravity flow to reduce the nitric acid concentration in the organic product stream (2DT) and, thus, minimize the volume of the final thorium nitrate product solution.

The 2DT overflowed the top disengaging section of the 2D Column to the bottom of the single-purpose 2E stripping column (T-K3). A dilute nitric (0.01 M) 2EX stream was added by gravity flow to the top of the column to strip (back-extract) the thorium from the organic. The organic waste stream (2EW) was routed to the No. 2 Solvent Treatment System. The thorium-bearing aqueous stream (2ET) was routed to the 2ET (E-K4) Concentrator by jet transfer (flow controlled by 2E Column (T-K3) interface recorder-controller). There, the 2ET was steam stripped and concentrated as required. The resulting bottoms solution overflowed the concentrator to TK-K5 where it was accumulated in batches for subsequent jet transfer to the Thorium Nitrate Product Tank (TK-K6). Here, the product was sampled and subsequently pumped to a tank trailer for transfer to the storage tank(s). The overhead condensate (2TD) from the 2ET (E-K4) Concentrator was routed to the 216-A10 process condensate crib for disposal.

SECOND AND THIRD URANIUM CYCLES (Slide 6)

The concentrated uranium stream from the Partition Cycle overflowed the 1CU (E-H4) Concentrator to Tank J1 where it was combined with the overhead condensate (3UD) from the uranium product concentrator. The solution was then pumped through a flow control system to the 2AF Feed Tank (TK-J21). From there, it was pumped through a second flow control system to the 2AF entry point about two-thirds of the way up the dual-purpose (extraction-scrub) 2A Column (T-J22).

The middle column differential pressure tap of T-J22 was utilized to add a concentrated nitric stream (12.2 M) near the feed entry point. The additional acid was required to prevent excessive uranium losses to the aqueous waste stream (2AW). This acid could not be added directly to the feed tank due to criticality prevention specifications which assumed an organic layer of 100 percent TBP in the tank. Minimizing the acid concentration also minimized the possibility of extracting excessive amounts of ^{233}U into such a TBP layer.

The 2AS scrub stream added to the top of the column contained ferrous sulfamate to reduce any residual plutonium to the nearly inextractable plus three valence. The uranium was extracted into the thirty volume percent TBP-NPH solvent (2AX) which entered the bottom of the column while the plutonium and most of the fission products exited via the aqueous 2AW waste stream. The 2AW stream was routed to TK-F10 in the Waste Concentration and Acid Recovery System for further processing and disposal.

The uranium-bearing organic stream overflowed the top disengaging section of the 2A Column to the bottom of the single purpose, stripping or back-extraction, 2B Column (T-J23). Here, a dilute nitric acid (0.01 M) stream (2BX) was used to remove the uranium from the organic. The resulting uranium-bearing aqueous stream (2BU) was jet transferred through a flow control system and sample pot to the Third Uranium Cycle feed tank. The stripped organic 2BW stream was recycled to the Partition (1BX) Column feed (1BSF) tank, TK-J3.

The flowsheet and operation of the Third Uranium Cycle was very similar to that of the Second Uranium Cycle. However, to maximize product purity, no ferrous sulfamate was added and distilled water was used in the preparation of the 3BX stream. In addition to providing decontamination from fission products, thorium, plutonium, and other metallic impurities, the Second and Third Uranium Cycle flowsheets resulted in a factor of 15 increase in the uranium concentration.

URANIUM-233 PRODUCT CONCENTRATION, LOADOUT AND STORAGE (Slide 7)

The 3BU stream from the Third Uranium Cycle flowed by gravity to the N Cell feed Tank, TK-N1. From TK-N1, the 3BU was pumped up through a cation exchange column, (T-N50, Figure 21), where any thorium present in the feed solution was preferentially absorbed onto the cation resin. The thorium-decontaminated column effluent (3CU) overflowed to the product concentrator, E-N6, for final concentration. After reaching the proper concentration (a volume reduction of a factor of 50), the concentrated product overflowed to the product receiver tank, TK-N7. Thirty liter product batches were accumulated in TK-N7, then vacuum transferred to the product sampling tank (TK-L9, Figure 29) in the PR Room. In TK-L9, the solution was well mixed and then sampled. Samples were taken using an air jet to circulate solution past a four-way sample valve inside the TK-L9 hood. Upon receipt of sample results, the product solution was vacuum transferred in 2.65 liter volumes to the loadout head tank, TK-L13. From L13, the uranium nitrate product solution was gravity loaded into tared three liter polyethylene bottles. Loaded bottles were capped, weighed, and then placed in either storage or shipping containers. The containers were closed and removed from the PR Room to temporary storage areas in the Purex Plant. The loaded containers were moved, via the PR truck, to the pipe gallery of the 221-U Building for storage and subsequent preparation for shipment offsite.

Primary differences between this process sequence and that used in 1966 were the elimination of the Vycor glass column used in 1966 for ²³³Pa decontamination, installation of the L9 product sampling tank for the 1970 Campaign, and the use of a new product loadout system.

WASTE TREATMENT AND ACID RECOVERY (Slide 8)

The waste treatment and acid recovery chemical flowsheet used was similar to that used in the 1966 Campaign. The main differences were:

1. The rerouting of the overheads during the feed concentration step from the waste concentrator feed tank (TK-F7) to the acid absorber bottoms (AAA) receiver tank (TK-F3); and
2. The utilization of TK-F18 for reverse strike waste neutralization and disposal to underground storage, rather than direct strike waste neutralization and disposal from TK-F16.

Rerouting of the feed concentrator overheads to the AAA receiver tank (TK-F3) permitted operation of the concentrator at optimum conditions for steam stripping of nitric acid without exceeding boiloff capacity. Despite the direct addition of the condensate into the 25 percent recovered acid, only a moderate rise in the recovered acid fission product content was noted. As previously stated, this was due to the long target cooling time prior to processing.

The aqueous waste streams from the extraction columns were collected and fed to the high level waste (1WW) concentrator (E-F6). The HAW stream gravity flowed directly to the feed tank (TK-F7). The 2DW, 2AW and 3AW streams flowed by gravity to TK-F10, combined with the vent system condensate and were pumped to TK-F7. A small stream of sugar solution was added to TK-F7 to suppress ruthenium volatilization from the concentrator. The combined waste was pumped from TK-F7 to the waste concentrator (E-F6). The overheads from the concentrator passed through an auxiliary demister and an acid absorber (T-F5). The bottoms

overflowed into the 1WW receiver tank (TK-F26) and was jetted in batches to the sugar denitration vessel and digested at elevated temperatures to destroy the remaining sugar and denitration byproducts. From TK-F16, the waste was jetted to TK-F18 for reverse strike neutralization* with 19 M sodium hydroxide (NaOH). The alkaline waste was then transferred to an underground storage tank.

The 25 weight percent nitric acid recovered in the F5 absorber tower (AAA) overflowed to TK-F3, was combined with the feed concentrator condensate, and was pumped to the vacuum fractionator feed tank (TK-U5). The vacuum fractionator concentrated the dilute nitric to 60 weight percent (13 M) for reuse, primarily in the dissolvers, as Purex recovered nitric acid.

NO. 1 AND NO. 2 SOLVENT TREATMENT SYSTEMS (Slides 9 and 10)

The chemical flowsheet for the No. 1 and No. 2 Solvent was essentially identical to the final flowsheet used in 1966 with the following exceptions: (i) the potassium permanganate concentration in the $\text{Na}_2\text{CO}_3\text{-KMnO}_4$ wash was reduced by one-third; (ii) the No. 2 Solvent (200) was not centrifuged; (iii) the acid content of the 200 was reduced during the 1970 Campaign; and (iv) the operating temperatures were reduced.

The organic waste stream (1CW) from the uranium stripping (1C) Column of the Co-Decontamination Cycle was washed with a $\text{Na}_2\text{CO}_3\text{-KMnO}_4$ solution in TK-G1. The aqueous stream was recycled by a pump at a high flow rate [200 gallons per minute (gpm)] for a period of eight to 12 hours and then changed out on a batch basis. The continuous organic stream was transferred to the bottom of the pulsed acid-wash (1O) Column via a pump with a short dipleg.

* Reverse strike caustic neutralization - addition of the acidic solution to the 19 M caustic. This method decreases the quantity of solids formed.

In the IO Column, the organic was contacted with a recirculating dilute nitric acid stream which was also changed every eight to 12 hours. A small amount of concentrated (12.2 M) nitric acid was added continuously at the top of the column to maintain stability. The solvent overflowed the column to the TK-G7 turbomixer where it was contacted with a continuous sodium carbonate stream. The aqueous waste was pumped to the first cycle combined solvent treatment waste (10W) storage tank (TK-G8) via the decanter (TK-G6) for subsequent batch transfer to underground storage.

The treated solvent was pumped to the 100 pump tank (TK-G5) where nitric acid was added during agitation of the vessel contents to assure that entrained sodium carbonate was not pumped to the solvent extraction columns. The acidified solvent was then pumped to the 100 header which supplied the Co-Decontamination and Partition, Second Uranium, and Third Uranium Cycles.

In the No. 2 Solvent Treatment System, the organic waste stream (2EW) from the Second Thorium Cycle received a carbonate-permanganate wash followed by a nitric acid wash prior to returning to the process as the 2DX stream. The equipment, flowsheet, and waste handling procedures for this system were as described for these operations in the No. 1 System, except a different type cartridge was used in the acid wash (20) Column, more acid was added to the top of the column to provide the desired 200 acid concentration and the No. 2 system did not have a turbomixer.

PERFORMANCE

Overall

The 170 thoria campaign was targeted to provide a minimum of 360 kilograms of high purity ^{233}U (as uranyl nitrate hexahydrate solution) for use in the Light Water Breeder Reactor (LWBR) program directed by the Division of Naval Reactors. As shown in the next slide (11), about 600 kgs of ^{233}U were recovered from approximately 470 tons of irradiated thoria target elements. The overall recoveries based on reactor input data were 95.2 percent for uranium and 94.9 percent for thorium.

The production goal was exceeded by about 35 percent as approximately 490 kgs of ^{233}U bettered all product specification requirements except for ^{232}U content which was determined by reactor operation. Approximately 40 percent of the thorium product met all specifications.

Head End Performance and Recovery Efficiencies (Slide 12) - Thoria Powder

The length of time required to process a powder charge was critical to maintaining the plant rate. Caustic de-jacketing of aluminum-clad elements is a standard Purex operation, and the normal three and one-half hour digest period proved to be adequate. Powder dissolution, however, required anywhere from 16 to 48 hours. During the latter half of the campaign, the dissolution time was arbitrarily set at 18 hours. An extra dissolution step (1,000-gallon heel cut) then proved to be necessary every third or fourth charge to dissolve residual thoria. The shortest cycle time (time required for complete processing of one charge in a dissolver) for a powder charge was about 30 hours. Most charges required between 30 and 35 hours. The extra heel dissolution step added 12 hours to the dissolver cycle. The decladding waste treatment cycle, which required 12 hours, excluding the digestion step, did not affect the overall dissolver cycle. Two centrifuge cakes were generally combined for the six-hour digestion period.

Material balances were calculated for powder charges after establishing the arbitrary 18-hour dissolution period. During dissolution, approximately 75 to 80 percent of the thoria charged was dissolved. Another five to 10 percent was recovered during decladding waste solution centrifugation.

Thoria Wafers

Approximately 58 tons of thoria wafers were processed through the C3 Dissolver during the "specification" portion of the campaign. The thoria wafers were processed through Head End using the same flowsheet and operating parameters used for powder except for changes made in the sparger operation during the dissolution step. The wafers dissolved much more rapidly than the powder. The

initial dissolution time of 18 hours was gradually decreased to between 10 and 12 hours without any significant heel buildup. With a dissolution time of eight hours an extra heel dissolution was necessary every fifth or sixth charge. For a 10 hour dissolution time, the overall cycle for thoria wafer processing was about 25 hours or equivalent to a 1.15 capacity factor (CF) rate.

Feed Concentration and Denitration

The feed concentration and denitration time cycle was adequate to provide feed for sustained solvent extraction operation at a 1.5 CF. Typical heat transfer coefficients (U values) ranged from about 170 BTU/hour-ft²-°F at low thorium concentrations to 115 BTU/hour-ft²-°F during the denitration step. The typical TK-D5 thorium and nitric concentrations were 1.4 M and 0.1 to -0.1 M, respectively. As a result, a butt of ten-to-twenty gallons of 19 M sodium hydroxide to TK-D5 was usually required to adjust the nitric acid concentration.

Co-Decontamination and Partitioning Cycle (Slide 13)

The HA Column operation presented no unusual problems during the campaign. Performance was satisfactory at the rates attempted. The thorium losses in the HAW stream were typically 0.01 to 0.1 percent of the HAF input. On several occasions (primarily during startups) the HAW thoria loss was as high as 0.4 to 0.6 percent of the input. However, during the period from November 25 to November 29, the ²³³U losses increased to 0.1 to 0.2 percent. Difficulty experienced in controlling the HAF flow during this period resulted in minor over-saturation of the organic (the thorium losses were also up slightly).

The steady-state performance of the Partition Cycle was satisfactory. Thorium loss to the uranium cycles was typically less than 0.01 percent of the input rate and the uranium loss to the thorium cycle was typically 0.01 to 0.05 percent. Uranium recycle via the 1BSU stream was normally 10 to 12 percent; however, it reached 60 to 70 percent during partitioning failures. Uranium losses in the 1CW organic waste stream ranged from 0.5 to 0.05 percent of the feed input. These losses were incurred even though the 1CX flow was increased by approximately 45 percent early in the campaign.

Fission product decontamination performance across the Co-Decontamination and Partition Cycles is summarized in the table below. The data are presented as decontamination factors, ratios of the fission product concentrations (micro-curies per pound thorium or gram ^{233}U) in the HAF versus the 2DF for thorium and the HAF versus 2AF for uranium.

	Co-Decontamination and Partition Cycle Decontamination Factors		
	<u>Zr-Nb</u>	<u>Ru-Rh</u>	<u>Pa</u>
Thorium	180	105	85
Uranium	3.2×10^4	115	5.0×10^4

Some minor flowsheet adjustments were made during the campaign in an effort to shift the ^{106}Ru split toward the uranium cycles where the ruthenium decontamination was more effective. These changes included the reduction in the 1BX Column aqueous-to-organic flow ratio (L/V), and increases in the 1BX HNO_3 concentration and the 1BS organic rate. No significant differences were noted.

The 1BXT flow rate proved to be rather limited with a maximum sustainable rate corresponding to a 1.05 capacity factor. However, since the head end rate (and also the Second Uranium Cycle rate on several occasions) was even more restrictive, the 1BXT flow limitation was not a problem.

Second Thorium Cycle (Slide 14)

Under normal conditions, the operation and performance of the Final Thorium Cycle was satisfactory throughout the campaign at rates up to 1.0 CF. The typical thorium losses in the 2DW and 2EW streams were less than 0.007 percent of the input during the early or "non-specification" portion of the run. However, the typical 2DW thorium loss increased to a range of 0.1 - 1.0 percent during the "specification" portion of the campaign. Even higher 2DW losses were experienced on several occasions. Typical thorium losses during the 1966 Campaign were 0.2 and less than 0.05 percent in the 2DW and 2EW streams, respectively.

The higher 2DW losses resulted from a deliberate increase in organic saturation which was made in an effort to improve the fission product decontamination attained in the 2D Column. This change was required due to a reduction in cooling time of the feed as the campaign progressed, resulting in a corresponding increase in fission product content.

The average (and range of) arithmetic decontamination factors, attained in the Final Thorium Cycle during the specification portion of the campaign were 150 (18-470), 12 (2.5-21), and five (1-15) for ^{95}Zr , ^{106}Ru , and ^{233}Pa . The protactinium decontamination during the processing of shorter cooled material at

the end of the campaign increased to the 500 to 2,700 range. This increased DF was due partly to a factor of 100 increase in the protactinium content of the 2DE and to the addition of phosphoric acid via the 2DIS stream. These DF's compare favorably with the typical DF's reported for the 1966 campaign of 7-8, 4-5, and 10 for zirconium, ruthenium, and protactinium, respectively.

Second and Third Uranium Cycle (Slide 15)

Generally, the operation and performance of the Second and Third Uranium Cycles were satisfactory through the campaign at rates up to 1.0 CF. The typical uranium losses in the 2AW and 3AW streams were 0.2 percent and less than 0.1 percent, respectively. Reported 2BW recycle rates averaged 1.0 percent during the early or "non-specification" portion of the campaign and decreased to 0.5 percent during the "specification" portion of the campaign. However, these numbers are believed to be biased high because of cross-contamination resulting from the use of the same sampling equipment for both the 1BXF and 2BW streams. Based on the flowsheet, the 2BW and 3BW uranium recycle rates should have been approximately equal.

The average (and range of) arithmetic decontamination factors attained in the Second and Third Uranium Cycles during the 1970 Campaign are shown and compared with the typical DF's reported for the 1966 Campaign in the table below. The comparison is favorable in all cases.

Second and Third Uranium Cycle Decontamination Factors

	<u>Second Cycle</u> 1970	<u>1966</u>	<u>Third Cycle</u> 1970	<u>1966</u>
$^{95}\text{Zr-Nb}$	400 (5-2800)	20	45 (0.3-186)	20
^{106}Ru	1700 (13-5300)	200	11 (1.3-24)	20
^{233}Pa	100 (< 1-550)	13-75	13 (1-168)	2-3

As was the case in 1966, accurate DF's could not be determined for thorium since the thorium concentrations in the uranium streams were nearly always reported as less than values. However, using these values would give indicated thorium DF's of 30, 45, and 1,350 for the Second Uranium Cycle, Third Uranium Cycle, and both systems, respectively.

^{233}U Concentration and Loadout (Slide 16)

1. T-N50 Cation Resin Column

The ion exchange column was bypassed during the high ^{238}U portion of the campaign. The high uranium holdup on the bed would have acted as a source of ^{238}U during subsequent specification grade ^{233}U production. During specification ^{233}U production, the column provided backup thorium separation. There was no difference in the thorium levels in the high ^{238}U product, approximately 2.8 kilograms of uranium were eluted from the bed, concentrated, and loaded out as product. This material met all product specifications except those for ^{232}U and phosphorous.

2. E-N6 - Product Concentration

The concentrator capacity was not overtaxed at ^{233}U production rates. During transition to rates near 1.0 CF, steam adjustments often required approaching maximum steam flow. Control of the N6 solution specific gravity was excellent. After an initial period of empirically determining the proper control point, product concentration was maintained at the flowsheet value with only minor difficulties.

3. Product Sampling and Loadout

The new L9 tank proved to provide excellent mixing and the L9 sampler was reliable, trouble-free, and no contamination problems were experienced with it. One problem with the sampler was that only two milli-liters of sample could be obtained with each turn of the sampler valve. As the required sample size gradually grew to 150 milli-liters, it required many turns of the sampler valve and about five minutes to take this sample.

The volume of product solution charged to a bottle had to be decreased to 2.65 liters, from the 2.9 liters used in 1966, due to smaller size bottles. The 2.9 liters filled the new bottles almost to the top of the neck. Some spillage occurred during the initial shipment which was attributed to jostled bottles. Decreasing the volume of solution per bottle was one remedy used.

In general, product sampling and loadout was trouble-free. On one occasion, about 200 milli-liters of solution overflowed a bottle to the floor of the loadout hood. The operating error came about through faulty communications between the individual at the L13 Tank and the individual at the loadout hood. The spilled solution and excess solution in the loadout bottle were transferred to a rework tank by means of the loadout hood vacuum transfer line. The loadout hood required extensive decontamination work.

Waste Concentration and Acid Recovery (Slide 17)

The performance of the waste concentrator and associated off-gas system was satisfactory. The F6 concentrator contributed little activity to the Purex recovered acid. Typical ratios of the $^{95}\text{ZrNb}$ and ^{106}Ru content of the bottoms to that of the condensate ranged between 10^4 and 10^5 .

The nitric acid boiloff in E-F6 was close to that predicted in the flowsheet. The bottoms acid concentration ranged between 3.7 M and 4.1 M versus a flowsheet value of 4.0 M. The control of the F6 concentrator bottoms overflow rate was poor, initially. Approximately 350 gallons of waste were generated for every ton of thorium processed during the non-specification portion of the campaign, versus a flowsheet value of 300 gallons per ton. Most of the excess volume was generated during the first two weeks of operation. During subsequent processing, the overflow averaged about 10 percent above flowsheet. The concentrator boiloff capacity was more than adequate for a 1.0 CF rate. This was the primary benefit derived from routing the condensate from the feed concentrator to the recovered acid system instead of to the waste concentrator feed tank (TK-F7).

The waste denitration and neutralization processes proved adequate. Sugar efficiency ranged between 14 and 15 moles of nitric acid destroyed per mole of sugar consumed. These values were typical for 1WW with a high aluminum nitrate content. Batch turnaround times in TK-F15 were satisfactory at a 0.75 CF rate, but marginal at a 1.0 CF rate. Some improvement in batch turnover was achieved by lowering the reaction temperature to accommodate higher sugar addition rates. However, at too low a temperature, this technique resulted in increased waste volume because the byproduct water was not boiled off. During the digestion period, some volume reduction was obtained which compensated for part of the increase during sugar denitration.

Caustic consumption during waste neutralization by reverse strike in TK-F18 was high during the non-specification portion of the campaign. The reported caustic ratios (pounds of 50 percent caustic required to neutralize one gallon of the sampled solution) were inaccurate. Further, the reported pH values of neutralized waste were difficult to correlate due to the complexity of the solution. An empirical curve was established which provided caustic ratios based on known aluminum nitrate concentration in the waste and the acid concentration measured in the laboratory. Improved control of caustic additions resulted, although caustic consumption continued to be excessive.

Performance of the T-F5 acid absorber was difficult to assess. The recovery efficiency was indirectly determined to be about 80 ± 5 percent. This recovery had been normal for the level of acid in the condensate samples during thorium operation. The efficiency and bottoms concentration could not be directly evaluated due to the influx of the feed concentrator (E-F11) condensate into TK-F3.

The acid vacuum fractionator operation was difficult to control at the required constant bottom acid concentration and production rate with minimal overhead loss. The difficulty was due primarily to the non-uniformity of the feed acid concentration and the wide variation in feed rate. The feed fluctuations were due to the batchwise denitration operations conducted in the feed concentrator. A nomograph was constructed which provided material balances around the fractionator for given operating conditions. Upon incorporation of the nomograph in the operating procedure and fractionator process control, the overall acid recovery rose from between 90 and 95 percent to 99.95 percent.

No. 1 and No. 2 Solvent Treatment Systems (Slide 18)

Operation of the Solvent Treatment Systems was generally satisfactory at rates up to 1.0 CF. Solvent quality was high throughout the campaign except during recycle or "spinning" of the solvent within the system. A comparison of the typical 1970 values for solvent plutonium retention and radionuclide content with those of 1966 is shown in the table below.

No. 1 and No. 2 Solvent Quality

	<u>No. 1 Solvent</u>		<u>No. 2 Solvent</u>	
	<u>1966</u>	<u>1970</u>	<u>1966</u>	<u>1970</u>
Pu Retention counts/min.-gal	1.5×10^6	2×10^6	2.5×10^6	6×10^6
Ru, $\mu\text{c/gal}$	50	200	40	13*
Zr, $\mu\text{c/gal}$	3	0.5	5	0.3*
Pa, $\mu\text{c/gal}$	15	0.2	50	0.3*

* Only three analyses reported.

The reduction in the zirconium and protactinium content of the 1970 solvent was probably due to the longer cooling time of the target elements prior to processing. The increased ruthenium content of the 1970 No. 1 Solvent did not significantly affect solvent extraction performance. Fission product decontamination factors across the Solvent Treatment Systems could not be calculated as gamma scan analyses of the 1CW and 2EW streams were not reported.

The average overall solvent loss during the 1970 thorium campaign was 585 gallons per operating day (gpd). This value was about a factor of three above the normal 150 to 200 gpd loss during uranium-plutonium processing and ten percent above the 530 gpd loss experienced during the 1966 Thorium Campaign. The solvent loss would have been even higher without the recovery of 20,000 gallons of solvent during the campaign which would have normally been discarded to waste.

PROBLEM AREAS (Slide 19)

Gaseous Effluents

Routine total alpha and total beta analyses of gaseous effluents were made during the thorium campaign. Both of these measurements increased above normal levels in the main building exhaust stream. Periodic checks disclosed that the majority of this abnormal activity had the short half-life characteristic of ^{212}Pb . The mechanism postulated involves the volatilization of ^{220}Rn (a daughter of ^{228}Th) from boiled or sparged process solutions. The 56-second half-life of the ^{220}Rn allowed only partial decomposition in the tank vapor spaces and off-gas lines. This permitted some of the ^{220}Rn to decompose downstream of the ventilation filters. Thus, the decomposition products were caught on the air samplers. Simple calculations based on plant inventory yielded approximate agreement with the measured releases. Calculations also indicated that the radionuclide concentrations at ground level did not exceed the limits for industrial exposure. However, some ^{103}Ru and $^{106}\text{Ru-Rh}$ were also emitted (probably from the acid boil-off system in the feed preparation cycle) and deposited on the ground which resulted in low-level ground contamination.

Partitioning Problems

On numerous occasions, the partitioning in the 1BX Column degenerated and a large percentage of the ^{233}U followed the thorium. The ^{233}U was generally re-extracted in the 1BS Column and recycled to the HA Column via the 1BSU-HAO stream. However, in the more severe cases, the ^{233}U continued on into the Final Thorium Cycle. A total of 20 to 25 tons of thorium product had to be reworked to lower the ^{233}U content as a result of these problems.

The partitioning problems were caused by two conditions: periodic high L/V ratios in the column; and loss of salting strength due to low thorium concentration in the 1BXF. Improved control of the 1BX L/V was gained in mid-October by installing a visual flowmeter and a pre-amplifier on the magnetic flowmeter signal output of the 1BX-H₂O system (demineralized H₂O).

The ²³³U tended to strip out of the organic whenever the thorium nitrate concentration in the 1BXF dropped. Startups and shutdowns unavoidably resulted in the thorium concentration being a factor of 10 to 100 below flowsheet. Recycled ²³³U from the Second and Third Cycles and any ²³³U being refluxed in the 1BX and 1BS Columns would immediately start stripping out into the thorium streams (1BXT and 1BT). This problem was reduced to a satisfactory level by doubling the 1BX-HNO₃ flow when low thorium concentrations were expected. The criticality prevention specifications for the 1BXF Tank (3,000 grams/ton) and the Final Thorium Cycle (500 grams ²³³U maximum) were violated on several occasions as a result of this problem. The specifications were subsequently changed.

Thorium-DBP Generation

One of the major reasons for the improvement in the 1C Column operation was the apparent reduction in the rate of thorium-DBP generation. The operating volume in the 1BXF Tank (TK-J3) was dropped by 50 percent, resulting in a reduction in organic residence/exposure time from 50 minutes to 25 minutes. The degradation of TBP from exposure to gamma radiation and nitric acid, and hence the amount of thorium-DBP formed, was reduced. The operation of the Second Uranium Cycle also showed significant improvement as a result of this change.

The Partition Cycle equipment was flushed four times during the campaign to remove thorium-DBP solids. Hot 57 weight percent HNO_3 was used to dissolve the solids and 500-gallon purges of organic were pulsed through the columns (with the HNO_3 still in) to "soak up" the dissolved thorium-DBP. The organic was then treated in TK-F13 to remove the contaminants before recycled to the solvent treatment system. The aqueous phase was routed to the Waste Concentration Acid Recovery System for nitric acid recovery, neutralization and disposal. The flushing cleaned out the columns quite efficiently.

Excessive Solvent Losses

Action taken to minimize solvent losses during the 1970 thorium campaign included installing a new aqueous selective jet for the TK-R1 to TK-R8 transfer, returning solvent from TK-R8 to TK-R1 for retreatment, and treating approximately 20,000 gallons of organic that would have normally been discarded to waste. However, in spite of these measures, the average solvent loss per operating day exceeded the normal value of 150 to 200 gpd for uranium-plutonium processing by nearly a factor of three at 585 gpd.

Measurement of the organic level in the underground organic wash waste receiver tank confirmed that this was the major loss point. Part of the losses can be attributed to excessive spinning of the solvent treatment systems while attempting to start up the solvent extraction systems. Prolonged startup delays due to problems in other areas of the plant resulted in spinning both solvent systems for approximately 40 days each.

2D Column Startup Problems - Phosphoric Acid Removal

Two attempts to start the 2D-2E Columns failed because of precipitation of a gelatinous material in the 2D Column. The precipitation was qualitatively identified as a thorium phosphate gel which would dissolve in 10 M nitric acid. The precipitate formed as a result of following the original startup procedure which called for establishing the column interface with the concentrated 2DF thorium (0.8 M) solution. The subsequent addition of phosphoric acid via the 2DIS stream resulted in the rapid formation of the thorium phosphate gel.

The Final Thorium Cycle columns were flushed with concentrated nitric acid following each of these startup attempts. The resulting flush solutions were jetted to the Waste Treatment and Acid Recovery System (TK-F10). Prior to the third startup attempt, the procedure was changed to call for the use of pulser water as the aqueous phase in establishing the interface and the phosphoric acid was removed from the 2DIS stream until increased protactinium decontamination was required. This early removal of phosphoric acid largely eliminated column instability problems in the Final Thorium Cycle experienced during the 1966 Thoria Campaign. In addition, the lower solids content of the 2EW organic waste stream contributed to improved operation of the No. 2 Solvent Treatment System.

Phosphoric acid was not added again until several tons of short cooled material were processed at the end of the campaign. At that time, the phosphoric acid content of successive 2DIS batch makeups was gradually increased until a concentration equal to 75 percent (0.50 M) of the flowsheet 0.66 M was reached. The use of phosphoric acid was largely responsible for the increased protactinium DF attained during this portion of the campaign.

Thorium Nitrate Product

With a few exceptions, the thorium product met the targeted specifications. The most significant exception was the ^{106}Ru -Rh content which averaged about 180 percent of the specification limit. As reported in the section on Normal Operating Performance and Capacity of the Final Thorium Cycle, the average ruthenium decontamination factor obtained across the Second Thorium Cycle was only 12. The ^{233}U content averaged below the 20 parts per million (ppm) limit but exceeded this by 75 percent in the storage tank containing the thorium product batches produced immediately following the start of the DNR or specification portion of the campaign. Also, the total uranium (excluding ^{233}U) content of the first thorium product was 63 ppm versus the target limit of 10 ppm. The contamination resulted from residual uranium held up in the Second Thorium Cycle equipment which was used for the Second Uranium Cycle during previous uranium-plutonium processing.

The reported analyses for the 1970 campaign compare reasonably well with the results reported for the 1966 campaign product. The higher fission product content of the 1966 product was primarily due to processing "hotter" feed. The higher ^{233}U levels for the 1970 campaign product resulted from partitioning problems associated with low salting strength in the 1BX Column (T-J6) during startup and shutdown periods.

The recorded Total Metallic Impurity (TMI) data were typical values based on results for individual product batches. A wide variation was noted in these results. For example, values exceeding 500 ppm thorium were reported for several elements (calcium, chromium, iron, magnesium, silicon) in some batches. Samples of the thorium product solutions in the storage tanks were not analyzed for TMI. Therefore, it was tentatively concluded that the iron content exceeds the 100 ppm specification limit.

CORROSION

Rust colored samples of two consecutive feed batches were obtained during the 1970 campaign. Based on an iron analysis, the first batch contained 156 pounds of iron which is equivalent to 220 pounds of stainless steel. Investigation revealed that this feed batch had been held in the feed concentrator for eight days at about 80°C. The second rust colored sample was apparently due to residue or "heel" remaining from the first batch. The color was judged due to dichromate solids.

The calculated uniform corrosion rate of the feed concentrator (E-F11) during this eight-day period was 9.5 mils per month. The total surface area in contact with the 1,700 gallons of solution was used in this calculation. The calculated corrosion rate using only the tube bundle surface was 16.8 mils per month. These values were not included when calculating the average tube bundle corrosion rate (2.5 mils per month) for the campaign.

Testing conducted following the thoria campaign indicated leaks in the coils of all three dissolvers. The holes were quite small as the leak rates at 90 psig were only 18, 7, and 16 gallons per hour for A3, B3, and C3 dissolvers. Although the increased corrosion due to the use of fluoride as required during the thoria and Zirflex campaigns may have contributed to these failures; inspection of one coil indicated mechanical failure due to thermal cycling stresses.

FUTURE PROCESSING RECOMMENDATIONS (Slide 20)

During the course of the campaign, various opportunities for process improvement were noted. Very few of these could be implemented because the press of production precluded time to complete the required development work. In addition, some problems arose which were not completely solved. These various aspects are discussed in the following paragraphs with the intent that these items be given consideration in the event that another thoria processing campaign is undertaken.

Wafers

The superior dissolution characteristics of the wafer targets makes these an obvious choice for a future run. Jet dipleg plugging was observed, and it is possible that partially dissolved wafers were drawn into the dipleg during solution transfer. It is suggested that a screen or other guard system be developed to reduce the likelihood of dipleg pluggage.

1C Cartridge

Even with the 1C Column (T-H3) cartridge essentially free of thorium-DBP solids, some evidence of instability was noted at a 0.85 CF. A new cartridge design is needed to provide improved capacity. This would allow a closer match of dissolution and solvent extraction capabilities.

Solvent Washing

The carbonate-permanganate wash solutions were changed on a fixed time basis. Changeout based on solution pH would probably save materials and waste volumes. In addition, particularly during pre-startup solvent spinning, some evidence was noted of significant permanganate leaving the 10 or 20 Column in the organic. When this permanganate decomposed to manganese dioxide solids, pluggage problems were noted on downstream filters. It also is possible that this contributed to high plutonium retention values. In any event, the need for permanganate or at least as much as was used is subject to additional study.

Ruthenium

Additional studies should be made to improve ruthenium decontamination in the solvent extraction battery and to reduce ruthenium volatilization from the feed denitration equipment. An alternate would be to route the denitration equipment off-gas to the Backup Recovery Facility.

Protactinium

The need for a protactinium removal step would be increased with shorter cooling times and should be reviewed in light of the requirements of the specific campaign.

Solvent Degradation

A modest change in the organic residence time under high acid conditions in the Co-Decontamination and Partition Cycle made a significant change in the deposition rate of thorium-DBP solids in the 1C Column. It is possible that further benefits such as the capability for processing shorter cooled targets could be obtained if the effect of thorium concentration, time, and acid concentration upon the degradation rate of TBP were known.

Also, the degradation of solvent in the 2A and 3A columns could be reduced if mixing pots were installed in the 2AF and 3AF lines. The pots would eliminate the need for adding concentrated acid solutions to organic continuous columns. It is felt that this practice contributed to the formation of thorium-DBP solids in the 2B and 3B Columns.

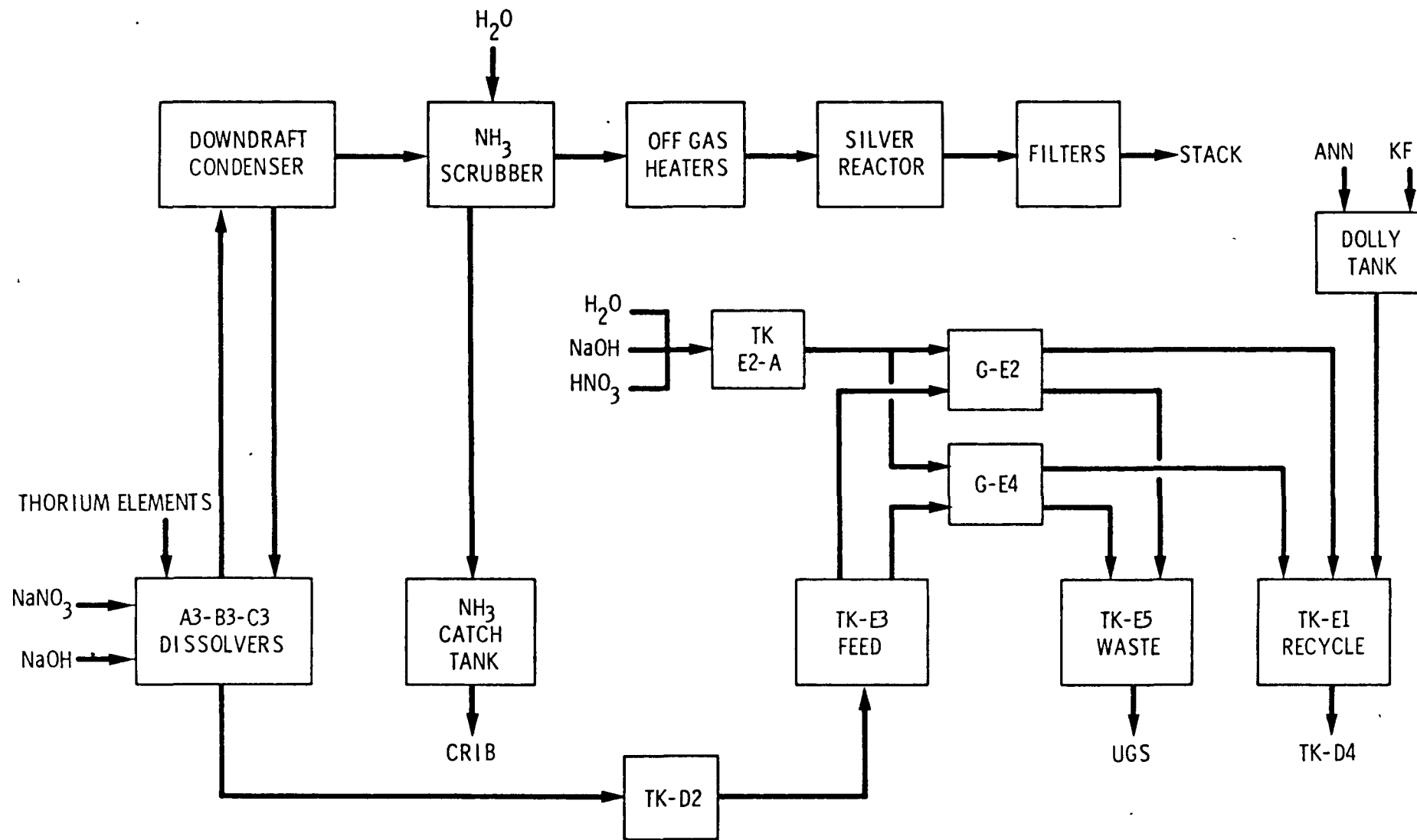
Third Plutonium Cycle

Use of the recently installed Third Plutonium Cycle Columns (T-L4 and L5) for the Third Uranium Cycle would eliminate the need to use J Cell Package columns (T-J22 and J23) for the Second Uranium Cycle. This change would be desirable as these columns are of marginal capacity for the flow required. In this scheme, the T-L1 and T-L2 Columns which were used for the Third Uranium Cycle in previous campaigns would be used for the Second Uranium Cycle. This change might result in fewer piping changes to conduct the campaign and some flowsheet changes to accomodate the equipment.

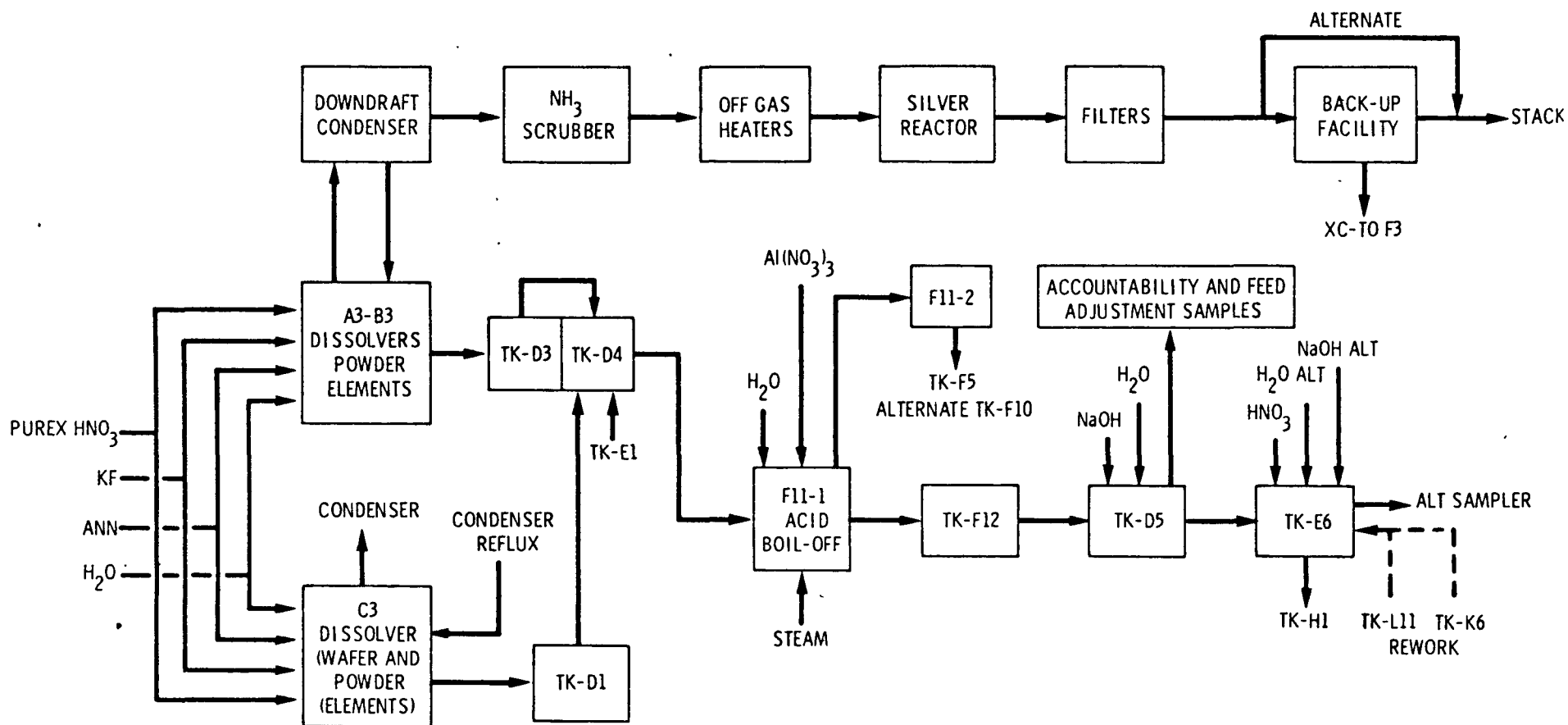
PLANT PREPARATIONS

1. PRE-SHUTDOWN ACTIVITIES
2. PLANT SHUTDOWN
3. PRODUCT RECOVERY FLUSHES
4. EQUIPMENT CHANGE-OUT
5. FINAL DECONTAMINATION FLUSHES
6. PLANT|OPERABILITY TESTING

COATING REMOVAL

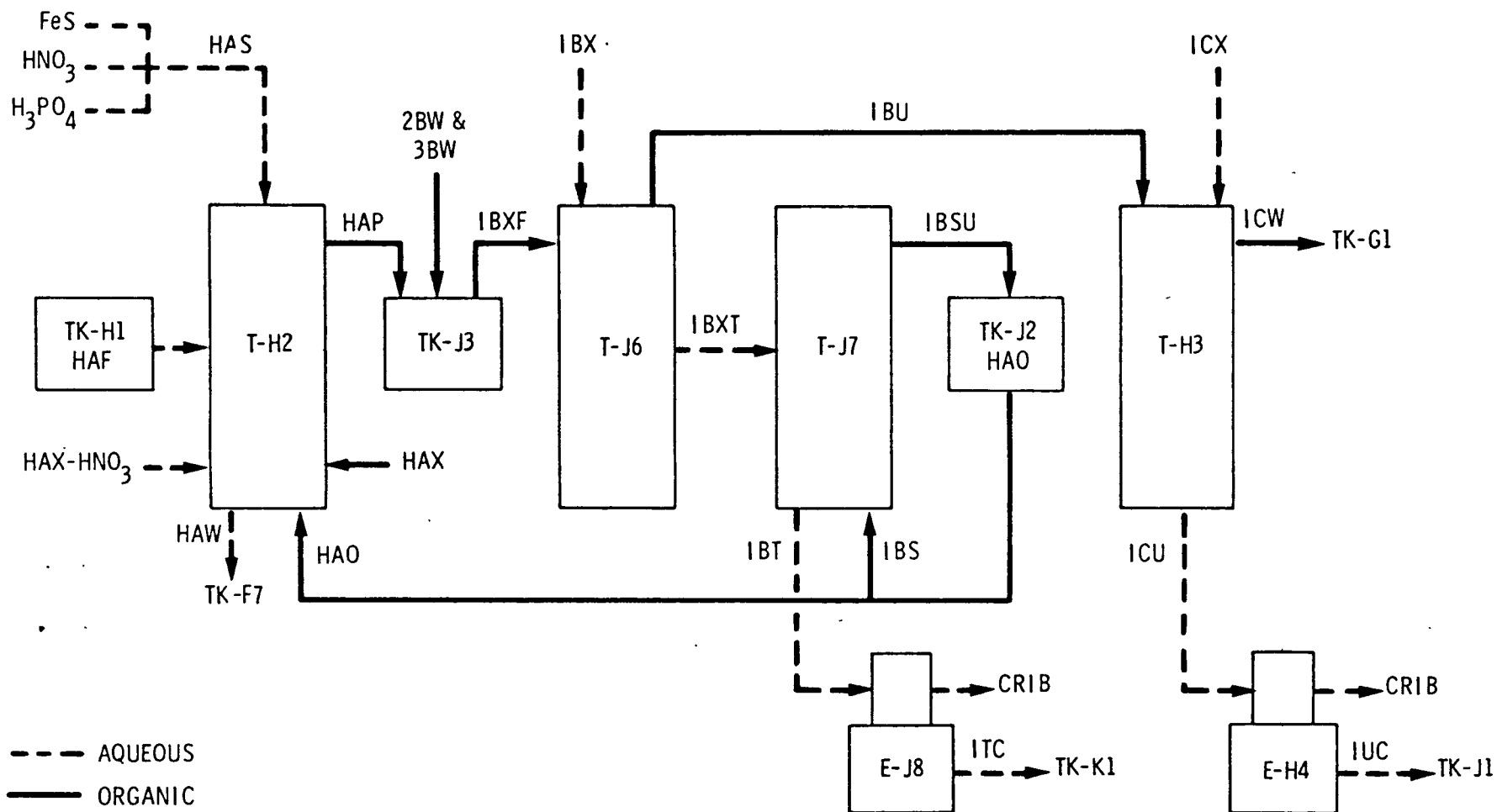


THORIA DISSOLUTION AND ACID REMOVAL

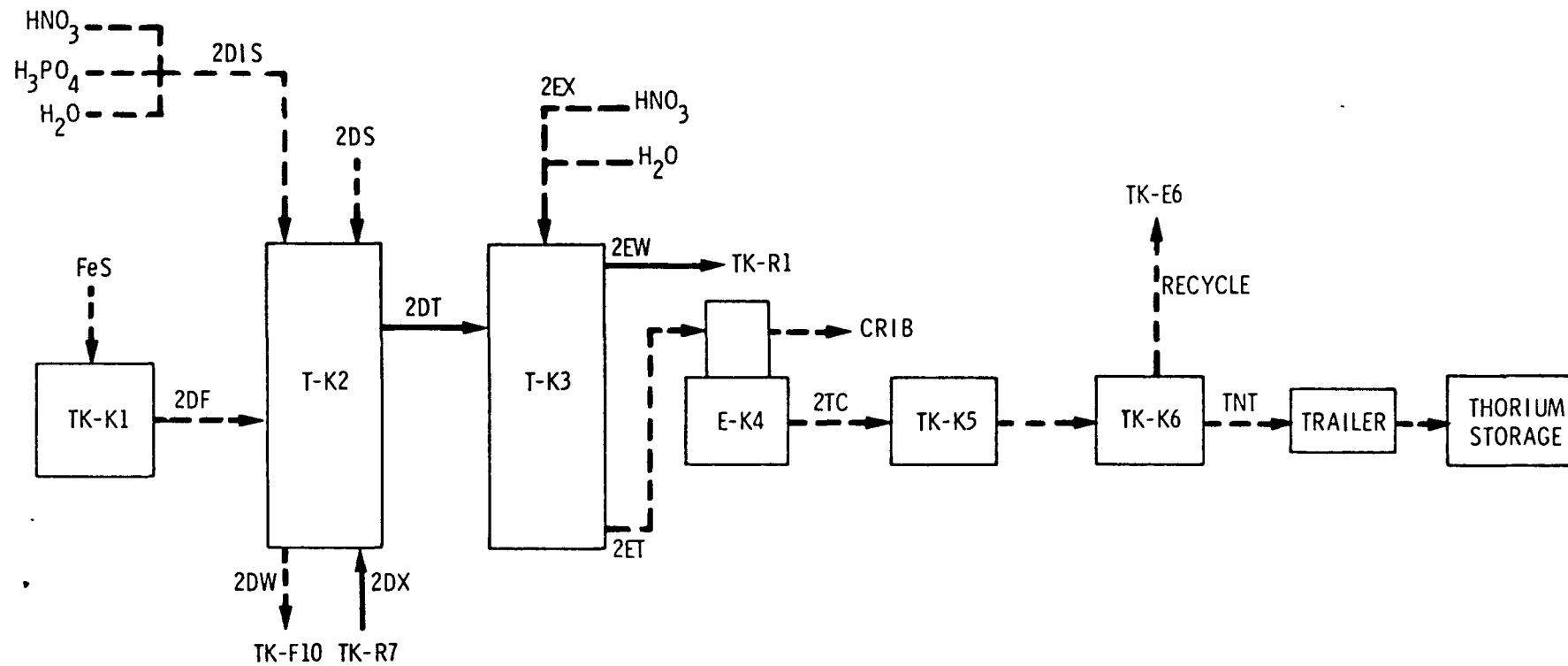


--- AQUEOUS

CO-DECONTAMINATION AND PARTITIONING CYCLE



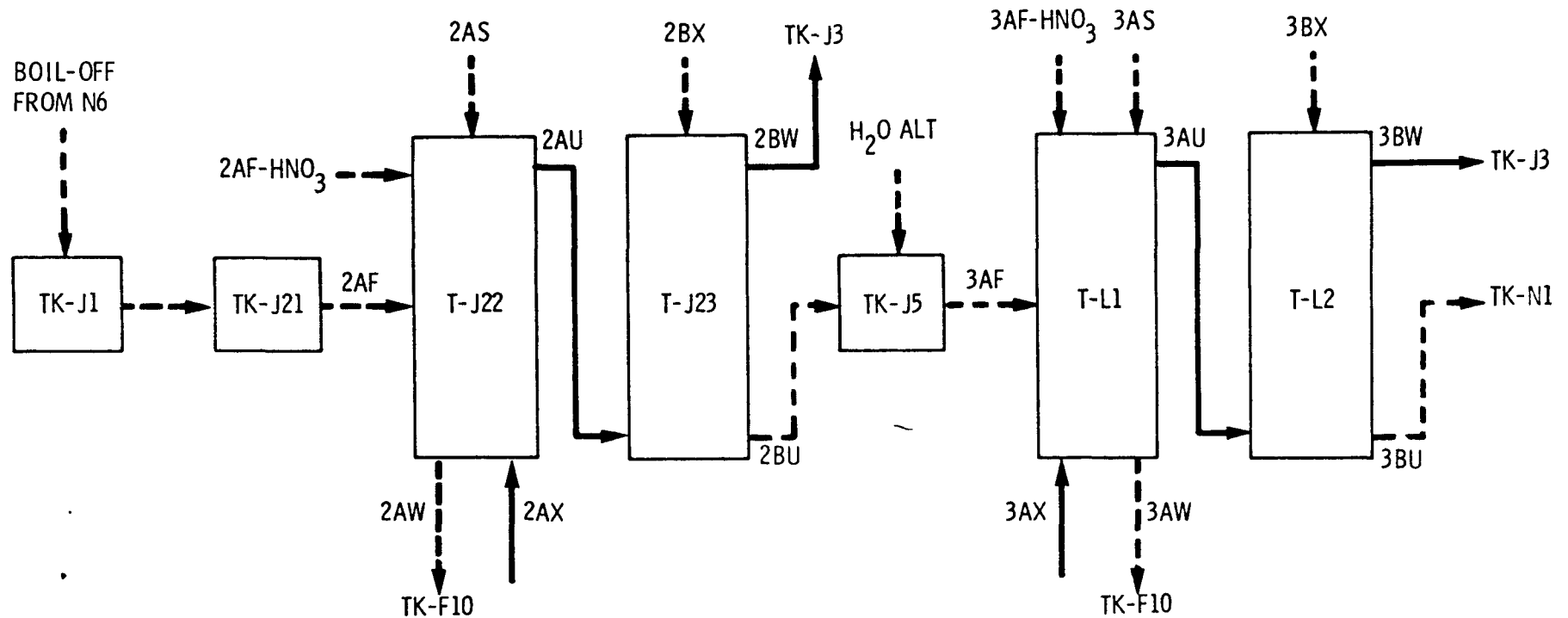
SECOND THORIUM CYCLE



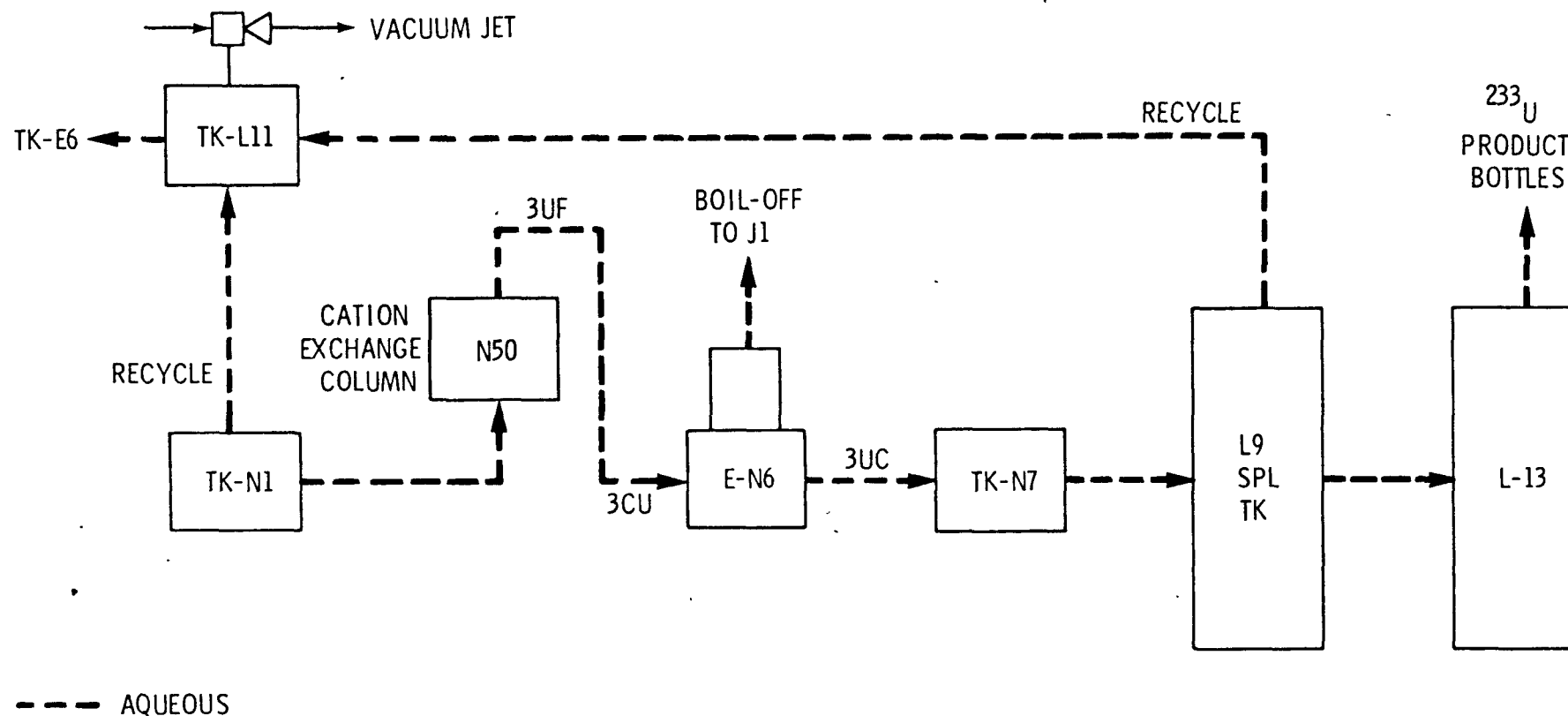
--- AQUEOUS
— ORGANIC

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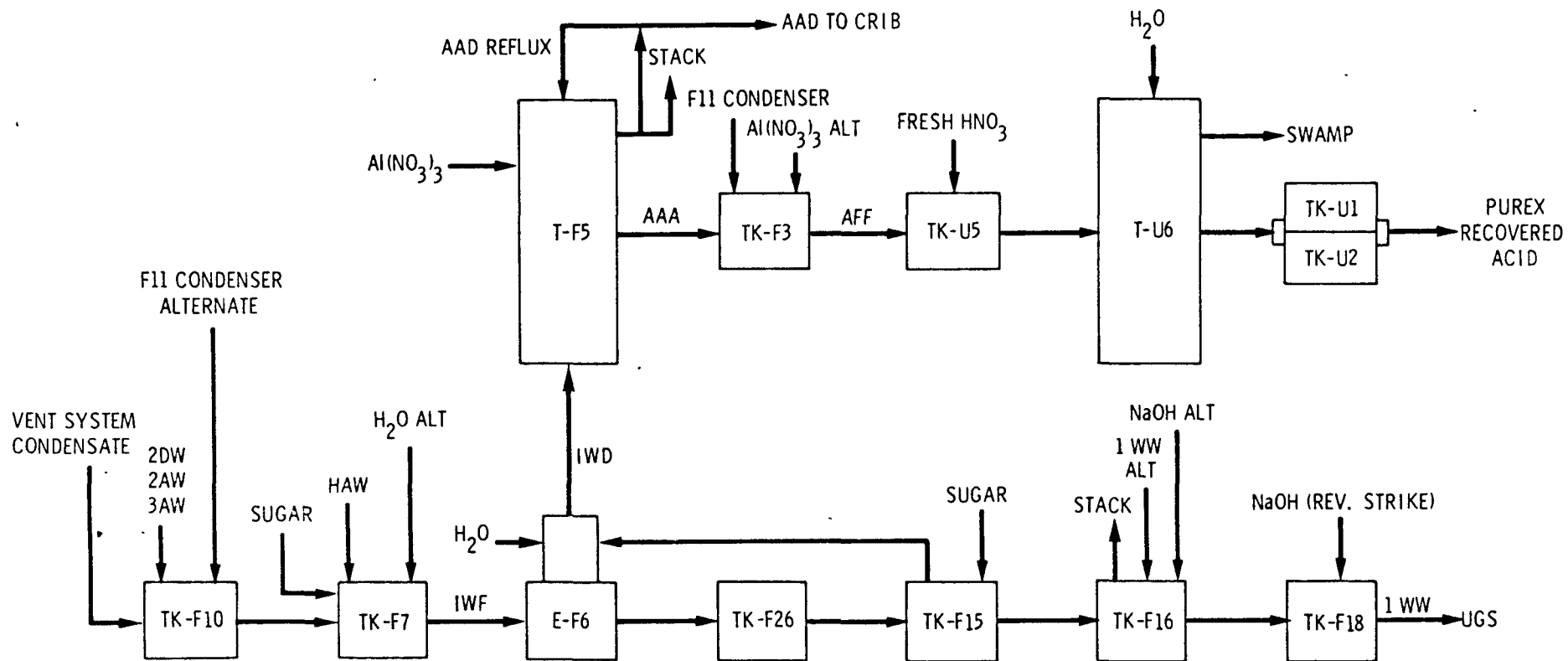
SECOND AND THIRD URANIUM CYCLES



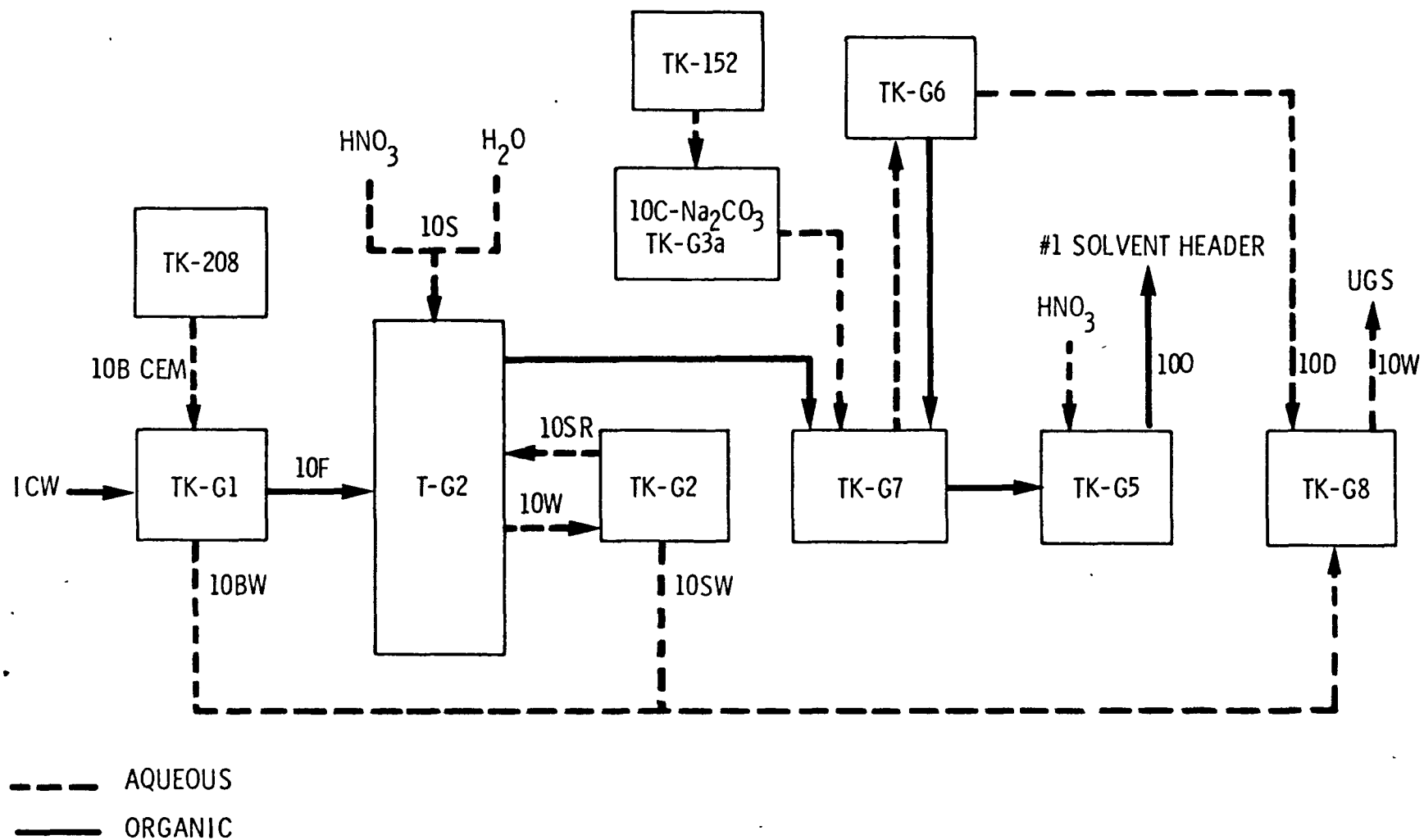
^{233}U CONCENTRATION AND LOADOUT



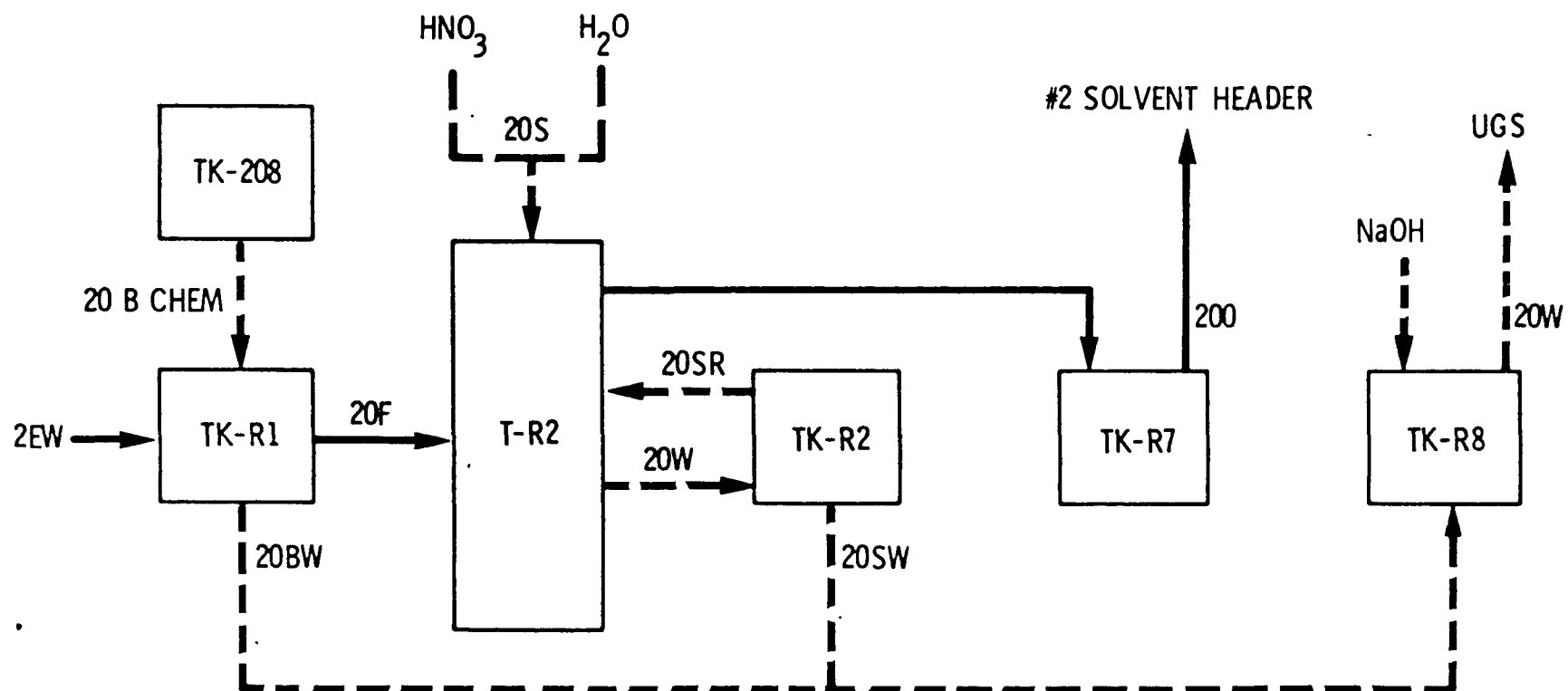
WASTE CONCENTRATION AND ACID RECOVERY



3



NUMBER 2 ORGANIC



--- AQUEOUS

— ORGANIC

1970 THORIA CAMPAIGN PRODUCT RECOVERY PERFORMANCE

	<u>INPUT</u>	<u>PRODUCT</u>	<u>% RECOVERY</u>
THORIA, tons	473.3		
THORIUM, tons	415.9	394.7	94.9
²³³ U, kgs	627.5	597.5	95.2

TYPICAL PERFORMANCE HEAD END

	<u>POWDER</u>	<u>WAFERS</u>
DISSOLUTION TIME, hrs	18	10
CYCLE TIME, hrs	30 TO 35	25
CAPACITY FACTOR	0.95 TO 0.81	1.15
HEEL CUT REQUIRED, CHARGE	3rd TO 4th	5th OR 6th @ 8 HOUR DISSOLUTION

TYPICAL PERFORMANCE / CO-DECONTAMINATION AND PARTITIONING CYCLE

	<u>THORIUM</u>	<u>URANIUM</u>
HAW LOSS, %	0.01 - 0.1	0.02 - 0.08
1BSU RECYCLE, %	---	10 - 12
1CW LOSS, %	---	0.05 - 0.5
DECONTAMINATION FACTORS		
$^{95}\text{Zr-Nb}$	180	3.2×10^4
$^{106}\text{Ru-Rh}$	105	115
^{233}Pa	85	5.0×10^4
THORIUM	---	10,000
URANIUM	6,000	
MAXIMUM RATE, tons / day	10.5	

TYPICAL PERFORMANCE SECOND THORIUM CYCLE

2DW LOSS, %	0.2 (0.007 - > 1.0)
2EW LOSS, %	0.01
DECONTAMINATION FACTORS	
⁹⁵ Zr-Nb	150
¹⁰⁶ Ru-Rh	12
²³³ Pa	5
MAXIMUM RATE, tons /day	10

TYPICAL PERFORMANCE

SECOND AND THIRD URANIUM CYCLES

	<u>SECOND CYCLE</u>	<u>THIRD CYCLE</u>
URANIUM LOSS, %	2 AW - 0.2	3 AW - 0.1
URANIUM RECYCLE, %	2 BW - 0.5	3 BW - <0.1
DECONTAMINATION FACTORS		
⁹⁵ Zr - Nb	400	45
¹⁰⁶ Ru - Rh	1700	11
²³³ Pa	100	13
THORIUM	30	45

^{233}U CONCENTRATION AND LOADOUT

- CATION RESIN COLUMN
- E-N6 CONCENTRATOR
- PRODUCT SAMPLING AND LOADOUT

WASTE CONCENTRATION AND ACID RECOVERY

- E-F6 CONCENTRATOR
- WASTE DENITRATION
- CAUSTIC ADDITIONS
- T-F5 ACID ABSORBER
- ACID VACUUM FRACTIONATOR

NO. 1 AND NO. 2 SOLVENT TREATMENT SYSTEMS

	<u>NO. 1 SOLVENT</u>		<u>NO. 2 SOLVENT</u>	
	<u>1966</u>	<u>1970</u>	<u>1966</u>	<u>1970</u>
Pu RETENTION, counts / min - gal	1.5×10^6	2×10^6	2.5×10^6	6×10^6
$^{106}\text{Ru} - \text{Rh}$, $\mu\text{c/gal}$	50	200	40	13*
$^{96}\text{Zr} - \text{Nb}$, $\mu\text{c/gal}$	3	0.5	5	0.3*
^{233}Pa , $\mu\text{c/gal}$	15	0.2	50	0.3*

*ONLY THREE ANALYSES REPORTED

PROBLEM AREAS

- GASEOUS EFFLUENTS
- PARTITIONING
- THORIUM-DBP SOLIDS
- EXCESSIVE SOLVENT LOSSES
- 2 D COLUMN STARTUP
- THORIUM NITRATE PRODUCT
- CORROSION

FUTURE THORIA PROCESSING RECOMMENDATIONS

- WAFERS
- RADON
- RUTHENIUM
- PROTACTINIUM
- SOLVENT DEGRADATION
- THIRD PLUTONIUM CYCLE
- 1C CARTRIDGE