

MAR 12 1964

CONF-322-3

2014

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December 10, 1963

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NEPTUNIUM RECOVERY AND PURIFICATION AT HANFORD

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ABSTRACT

Neptunium is routinely recovered from irradiated fuel elements at Hanford's two main separations plants. Initial development tests were started in the Purex plant in 1958, then in the Redox plant in 1959, and recently culminated in the installation of new production systems in both plants for improved recoveries. Both recovery flowsheets employ solvent extraction techniques based on the relative extractability of neptunium-VI. The neptunium is co-extracted with uranium and plutonium in the plants' first extraction cycles and then partitioned and decontaminated in separate neptunium cycles. Excellent decontamination from fission products is achieved without interfering with mainline uranium and plutonium production. Recovered neptunium is purified by anion exchange and shipped offsite for subsequent irradiation to plutonium-238. Overall separation factors of uranium and fission products from neptunium are greater than 10^7 and 10^{10} respectively.

NEPTUNIUM RECOVERY AND PURIFICATION AT HANFORD

INTRODUCTION

New process systems have recently been installed in Hanford's Purex and Redox plants to permit continuous production-scale recovery of neptunium-237. Neptunium is formed in Hanford's nuclear reactors as a by-product of plutonium-239 production and is recovered and purified in the chemical processing plants for subsequent conversion to plutonium-238.

The production reactor and chemical processing complex at Hanford is operated by the General Electric Company under prime contract to the U. S. Atomic Energy Commission. The Purex and Redox plants employ solvent extraction systems to separate and decontaminate plutonium from irradiated uranium for subsequent use in weapons components. The irradiated uranium is recovered and decontaminated from fission products for reuse in the U²³⁵ fuel and weapons systems. Recently the Purex plant has also been employed for recovery of useful fission products, including strontium-90, cesium-137, cerium-144, promethium-rare earths and technetium-99.

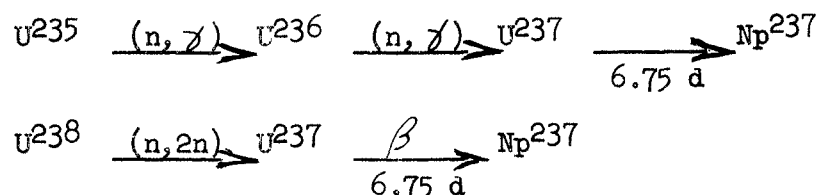
Recovery of the transuranic neptunium-237 was started at Purex in 1958 and at Redox in 1959 using main-line process equipment with special campaign operations for decontamination of accumulated material (Ref. 1, 2, 3). The use of the main plant system permitted rapid response to the AEC's early program needs for plutonium-238 in space power units. Increasingly higher demands for neptunium prompted a follow-up program to permit efficient and economical recovery on a continuing basis.

The following paper describes the new process systems recently installed at Hanford and summarizes program activities and process performance results to date.

FORMATION OF NEPTUNIUM

Neptunium-237 is a long-lived transuranic isotope formed by two reactions in the neutron irradiation of natural and slightly enriched uranium as shown in Table I.

TABLE I
NEPTUNIUM FORMATION



Most of the neptunium is formed by reaction of U^{238} with fast neutrons. Smaller amounts are formed by slow neutron capture in U^{236} since appreciable amount of U^{236} are generated in the system by neutron capture in U^{235} . The bulk of the U^{236} formed in the irradiation of natural uranium is lost to the reactor cycle when uranium is processed through the gaseous diffusion plants for isotopic enrichment. Hanford is participating in an AEC program to increase neptunium production by recycling the slightly enriched uranium stream from the reactors without processing in the cascades. Most of the U^{236} formed in the slightly enriched uranium is thus available for neutron capture in the reactors and increased overall yield of neptunium-237. In either case, the concentration of neptunium in uranium is very small so that recovery of gram quantities in the huge separations plants is a difficult and challenging assignment.

NEPTUNIUM RECOVERY AT PUREX

The process scheme used for the recovery of neptunium in Hanford's Purex plant is shown in Figure 1. After dissolution in nitric acid, the neptunium is extracted into the 30 per cent TBP-kerosene solvent along with uranium and plutonium in the HA Column and is scrubbed for fission product removal in the HS Column. The plutonium is partitioned into an aqueous phase in the IBX Column and the neptunium and uranium co-stripped in the IC Column. The IC product is concentrated and uranium is re-extracted in the 2D Column. The neptunium, however, is forced into the 2D raffinate stream which is concentrated for backcycle to the HA Column. Approximately one-third of the backcycle stream

is continuously processed through the new 3A Column where the neptunium is extracted into the organic phase. The neptunium is stripped in the 3B Column and returned to the 3A Column. Neptunium is thus accumulated in the 3A and 3B systems and is periodically decontaminated and removed to the new batch ion exchange unit for final purification and loadout.

The purpose of the 3A and 3B Columns in the plant is to permit continuous recovery of the neptunium and decontamination for purification without shutting down plutonium production operations. Without the new columns, neptunium can be accumulated in the uranium extraction and waste backcycle systems but can be decontaminated for removal only by special campaign processing through the plutonium decontamination system. This requires shutdown of essentially all normal process activities. In addition, accumulating the neptunium inventory within the main process system involves constant exposure to process upsets and losses of the inventory to waste streams requiring expensive and time consuming rework. The new solvent extraction battery thus permits improved plant operating efficiency.

The recovery flowsheets are based on control shifting of the neptunium between its three valence states and the relative extractability of each into the plant solvent. The process was developed in laboratory minimixer studies at Hanford using some of the valence control techniques discovered at Savannah River Laboratory (Ref. 3, 4). As shown in Figure 2, neptunium-VI is more extractable in 30 per cent TBP than neptunium-IV at low acidities while at high acidities, both are comparable. Neptunium-V on the other hand is virtually inextractable. The valence state of neptunium is controlled by the use of HNO_2 for catalytic oxidation to neptunium-VI and by the use of ferrous sulfamate for reduction to neptunium-IV. Thus the neptunium is extracted as neptunium-VI in the HA Column by oxidation with 0.005 M HNO_2 in the solvent. It is reduced to neptunium-IV in the IBX Column and maintained as neptunium-IV in the 2D and

3A Columns by ferrous sulfamate. The neptunium-IV is kept in the organic phase in the IBX Column by virtue of the low aqueous to organic flow ratio but is partitioned into the aqueous phase in the 2D Column by the high saturation of uranium in the solvent.

Flowsheet compositions for the 3A-3B systems are shown in Figure 3 for the accumulation phase of operation. Process specifications for the two columns and unique features of the equipment design are described in a separate paper (Ref. 5). During the accumulation phase, the partition demands on the system are three-fold - separation of plutonium and fission products from the neptunium in the 3A Column and separation of uranium from the neptunium in the 3B Column. The 3A Column feed is maintained at a high nitric acid concentration to assure good extraction of neptunium-IV. The scrub solution is a high acid-ferrous sulfamate-hydrazine solution to reduce plutonium to the inextractable plutonium-III for discharge to the raffinate. Feed flow is adjusted so that the uranium concentration in the solvent phase is ≤ 0.2 M to prevent high neptunium losses to the raffinate. The 3B Column back-extractant flow is maintained at one-third the solvent flow to strip out the neptunium into the aqueous phase while at the same time retaining uranium in the solvent for backcycle to the IBX Column feed stream in the main plant. The 3A Column raffinate is returned to the Backcycle Concentrator feed stream in the main process where the hydrazine is destroyed by nitrite reaction.

After a specified amount of neptunium is accumulated in the system, the decontamination phase of operation is started as shown in Figure 4. The backcycle stream is all processed in the HA Column and a synthetic feed solution is prepared for the 3A Column containing 4.5 M nitric acid. The 3A Column scrub is reduced in acid and salt content and the solvent flow decreased to improve fission product decontamination. The neptunium is then refluxed through the system until the separation from plutonium, uranium and fission

products is sufficient for the ion exchange purification step at which point the product flow is diverted to the ion exchange feed concentrator.

Performance of the system has been excellent with stable operation in the 3A and 3B Columns at volume velocities matching Semiworks Operation as shown in Table II (Ref. 6, 7). Instantaneous neptunium losses to the 3A and 3B raffinate streams have been less than 0.5 per cent at flowsheet conditions. Decontamination factors across the system are summarized in Table III for the extraction, accumulation and decontamination phases of the overall operation. The shifts in instantaneous DF for Zr-Nb-95 and Pu-Rh-103-106 between the accumulation and decontamination phases reflect the changes in feed and scrub acidity and the solvent flows. Performance of a typical decontamination run is shown in Figure 5 as a plot of relative 3B Column product activity levels vs. 3A Column feed throughput.

Integration of the neptunium recovery system into the main-line process has been smooth. The main effects were changes in the composition of the concentrated backcycle stream, addition of nitrite to the backcycle concentrator feed and backcycle of the 3B Column raffinate to the IBX Column feed stream, all of which were accomplished with no adverse effects on process efficiency. Overall recovery capabilities for the plant are greater than 80 per cent with carryover to the 2EU uranium product stream less than 10 per cent and losses to the 3A Column raffinate stream less than 10 per cent. Overall separation of the uranium and fission products from neptunium, based on 3A Column feed concentrations, is $>10^6$ DF for uranium, $>10^8$ for Pu-Rh-103-106, and $>10^9$ DF for Zr-Nb-94.

NEPTUNIUM RECOVERY AT REDOX

The process schemes used for recovery of neptunium in Hanford's Redox plant are shown in Figures 6 and 7. In the first scheme, neptunium is extracted and accumulated in the original equipment system and periodically decontaminated for removal by special campaign processing through the plutonium decontamination

system. The second scheme is based on routine decontamination of neptunium through use of plutonium solvent extraction columns made available by the installation of a continuously operated prototype anion exchange contactor for plutonium decontamination. In both cases, the neptunium is extracted into the hexone solvent along with uranium and plutonium in the precycle column system and is forced into the aqueous raffinate stream separate from uranium and plutonium in the partition column system. The neptunium is accumulated by recycling between the two systems and is periodically removed to a plutonium column system for decontamination.

The recovery flowsheets are based on aqueous-phase acid control and the relative extractability of neptunium-VI from acid ANN solutions as compared to acid-deficient ANN solutions as shown in Figure 8. The Redox process was converted from an acid-deficient feed system to an acid feed system to permit neptunium recovery (Ref. 3). Ruthenium decontamination is better, however, with an acid deficient system so that the partition and remaining cycles remain acid deficient. Thus, the neptunium, which is oxidized to neptunium-VI in the feed with dichromate, is extracted in the first cycle and is not extracted in the partition cycle.

In Figure 6, the neptunium from the IA Partition Column is returned to the HA Extraction Column where it is subject to potential losses to waste as it is re-extracted for accumulation. Therefore, in Figure 7, the neptunium is returned to the IS Column for accumulation and the raffinate is backcycled to the HA Column, thereby minimizing potential loss.

After a specified amount of neptunium is accumulated in the IS-HC Column system, the inventory is removed by a special water strip through the IS Column scrub section and is transferred to the 3A and 3B Columns previously used for plutonium decontamination. The neptunium is partitioned from residual uranium and plutonium by contact in the 3A Column from an acid deficient feed thereby extracting the uranium and plutonium and segregating the neptunium in the

raffinate. The neptunium is then extracted from an acid dichromate feed in the 3A Column, stripped in the 3B Column and ozonated batchwise for final ruthenium decontamination. If further decontamination is required, the process steps are repeated as necessary. The neptunium product solution is then concentrated and loaded out for final purification by ion exchange at the Purex plant.

Reserving the 3A and 3B Columns for neptunium decontamination rather than plutonium processing, minimizes the number of process operations otherwise required during campaign processing through the 2A-2B plutonium columns, eliminates the need for plant down-time to decontaminate the neptunium, and thus permits improved overall plant operating efficiency.

Performance of the system has been good with stable operation of the special purpose columns and smooth integration of the overall process system. Overall neptunium recovery capabilities for the Redox plant are greater than 90 per cent with essentially no carryover to the 3EU uranium product stream and losses to the HA Column raffinate stream of less than 10 per cent. Overall separation of the uranium and fission products from neptunium, based on HA Column feed concentrations are $>10^6$ DF for uranium, $>10^6$ DF for Ru-Rh-103,106 and $>10^8$ DF for Zr-Nb-95.

NEPTUNIUM PURIFICATION AT HANFORD

The neptunium recovered in the Purex and Redox plants is purified by batch anion exchange using the flowscheme shown in Figure 9.

The neptunium product solution from the Purex solvent extraction battery is steam-stripped and concentrated in a thermosyphon concentrator. The neptunium is then adjusted to neptunium-IV with ferrous sulfamate, stabilized with hydrazine and is loaded on an anion exchange resin column in a concentrated nitric acid medium. The product from the Redox system is adjusted in feed composition and loaded on the resin column without prior concentration in the exchange cell. Once loaded on the resin, the neptunium is first washed with concentrated

nitric acid containing HF to remove fission products. Residual fluoride is washed out of the column and the neptunium is eluted with dilute nitric acid. The concentrated portion of the eluant is diverted into a product tank where the neptunium is converted to the stable neptunium-V valence state and the product is then bottled for shipment offsite.

The purpose of the neptunium purification facility is to provide sufficient clean-up and concentration of the neptunium so that shipment of the product offsite can be done safely and economically. Without such a system, shipment of a uniform product from the two recovery systems could not be assured and development of alternate recovery processes would be restricted. Dilute product concentrations and higher fission product levels would involve considerably larger and uneconomical, heavily shielded shipping containers.

The purification flowsheet is based on the formation of stable anionic neptunium-IV complexes in concentrated nitric solutions and the high loading capacities of certain anion exchange resins for such complexes. The basic exchange technique was developed at Stanford and the process used in the new facility was thoroughly tested in semiworks systems (Ref. 8, 9). Control of the neptunium-IV valence in the high acid solution involves using ferrous sulfamate with hydrazine as a holding reductant. The use of small concentrations of HF permits relatively large fission product decontamination factors but requires extra steps for control. Controlled product elution permits recycling of dilute portions of the eluate and loading out only concentrated product so that a final concentrator system is not required.

Flowsheet compositions for the various steps in the purification process are shown in Table IV. Unique features of the equipment design are discussed in a separate paper (Ref. 10). The neptunium-IV is loaded on the resin at a temperature of 25°C and the relatively low rate of 8 milligrams neptunium per minute per square centimeter. Most of the plutonium loads simultaneously even though the

prevalent plutonium valence state in the feed is Pu-III. Plutonium is removed from the column at a temperature of 20° C by scrubbing at 4 milliliters per minute per square centimeter. A 20-column volume fission product scrub is passed through the resin at 4 milliliters per minute per square centimeter at 70° C. Product elution is performed at ambient temperature using 0.3 M nitric acid. The first 2 column volumes are recycled to the feed so that a net neptunium concentration of 35 to 45 grams per liter can be maintained for final valence adjustment and loadout. The wastes from the loading and washing steps are treated with nitrite to destroy the hydrazine and with aluminum nitrate to complex the fluoride before entering the backcycle concentrator in the main process sytem.

Performance of the system has been good with flowsheet loading and concentration values readily achieved (Ref. 11). The neptunium loading on the resin has approached 70 grams per liter. Decontamination factors for uranium, plutonium and fission products are summarized in Table V. Product elution and fission product scrubbing can be controlled by the use of a gamma scintillation monitor located in the resin outlet line. Bed gassing is controlled by periodically venting the system using a sonic probe to determine resin level and the presence of gas pockets.

SUMMARY

The installation of new process systems in Hanford's Purex and Redox plants permits the continued recovery and purification of neptunium-237 from irradiated uranium as a co-product of plutonium-239. The complex solvent-extraction systems of the chemical processing plants have been suitably modified to incorporate the new recovery processes. Performance of the new equipment has been excellent, meeting both flowsheet and design expectations. Integration into the main plants have been smooth with overall separation of uranium from neptunium and fission products from neptunium exceeding DF's of 10^7 and 10^{10} respectively.

ACKNOWLEDGEMENTS

Key chemists and engineers in the start-up of the new process systems and preparation of this paper include J. S. Buckingham, J. P. Duckworth, R. W. Lambert, S. M. Nielson, G. A. Nicholson, H. P. Simonds, and R. A. Yoder.

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TABLE II
NEPTUNIUM COLUMN PERFORMANCE AT PUREX
FLOODING LIMITS

	3A Column		3B Column	
	Vol. Vel. Gal-Hr ⁻¹ -SqFt ⁻²	Freq. Cyc-Min ⁻¹	Vol. Vel. Gal-Hr ⁻¹ -SqFt ⁻²	Freq. Cyc-Min ⁻¹
Cold Semiworks	1350 2200	85 70	1350 2000	77 ^(a) 70 ^(a)
Purex Cold Tests ^(b)	2150	78	1000	80
Purex Hot Tests				
Accumulation	1350 2200	95 78	1300	75
Decontamination	1600	75	1000	80

Notes: (a) The cold semiworks 3B studies were made at an amplitude of 0.6 inch. The frequency listed was corrected for the 0.75 inch amplitude in the plant 3B Column. All 3A studies were at an amplitude of 1.1 inch.

(b) The Purex cold tests were made using 5.6 M HNO₃ as the 3AF and solvent from the Purex No. 1 Solvent System as the 3AX.

TABLE III
NEPTUNIUM COLUMN PERFORMANCE AT PUREX
DECONTAMINATION FACTORS

<u>Cycle</u>	<u>Zr-Nb-95</u>	<u>Ru-Rh-103, 106</u>	<u>U</u>	<u>Pu</u>
<u>Typical Instantaneous DF's</u>				
Extraction	8000	600	100	*
Accumulation	10	10	3	20
Decontamination	20	20	30	∞
<u>Typical Cumulative DF's</u>				
Extraction	8000	600	100	*
Accumulation	1500	1500	400	2000
Decontamination	<u>100</u>	<u>100</u>	<u>150</u>	<u>∞</u>
Overall	1×10^9	1×10^8	5×10^6	*

TABLE IV
NEPTUNIUM BATCH PURIFICATION AT PUREX
FLWSHEET AND PERFORMANCE DATA

<u>Step</u>	<u>Composition</u>	<u>Volumes & Rates</u>	<u>Np to Backcycle</u>
Loading	6.0 M HNO_3 0.1 M FeSA 0.1 M N_2H_4	8 mg Np/min cm^2	1.0%
Pu Scrub	6.0 M HNO_3 0.1 M FeSA 0.1 M N_2H_4	15 - 20 col. vol. 4 ml/min cm^2	1.5%
FP Scrub	8.0 M HNO_3 0.05 M N_2H_4 0.01 M NaF	15 - 20 col. vol. 4 ml/min cm^2	2.0%
F Scrub	8.0 M HNO_3	1.5 col. vol.	\angle 0.2%
Forecut	0.35 M HNO_3	2 col. vol. 1 ml/min cm^2	5% (to 3XF)
Product	0.35 M HNO_3	1 col. vol. 1 ml/min cm^2	-

TABLE V
NEPTUNIUM BATCH PURIFICATION AT PUREX
DECONTAMINATION FACTORS

	<u>Typical DF's</u>	<u>Range of DF's</u>
Zr-Nb-95	1000	100 - 1500
Ru-Rh-103, 106	500	5 - 50,000
U	1500	10 - 10,000
Pu	200	3 - 300
TMI	80	60 - 100

FIGURE 1

NEPTUNIUM ACCUMULATION – PUREX PROCESS

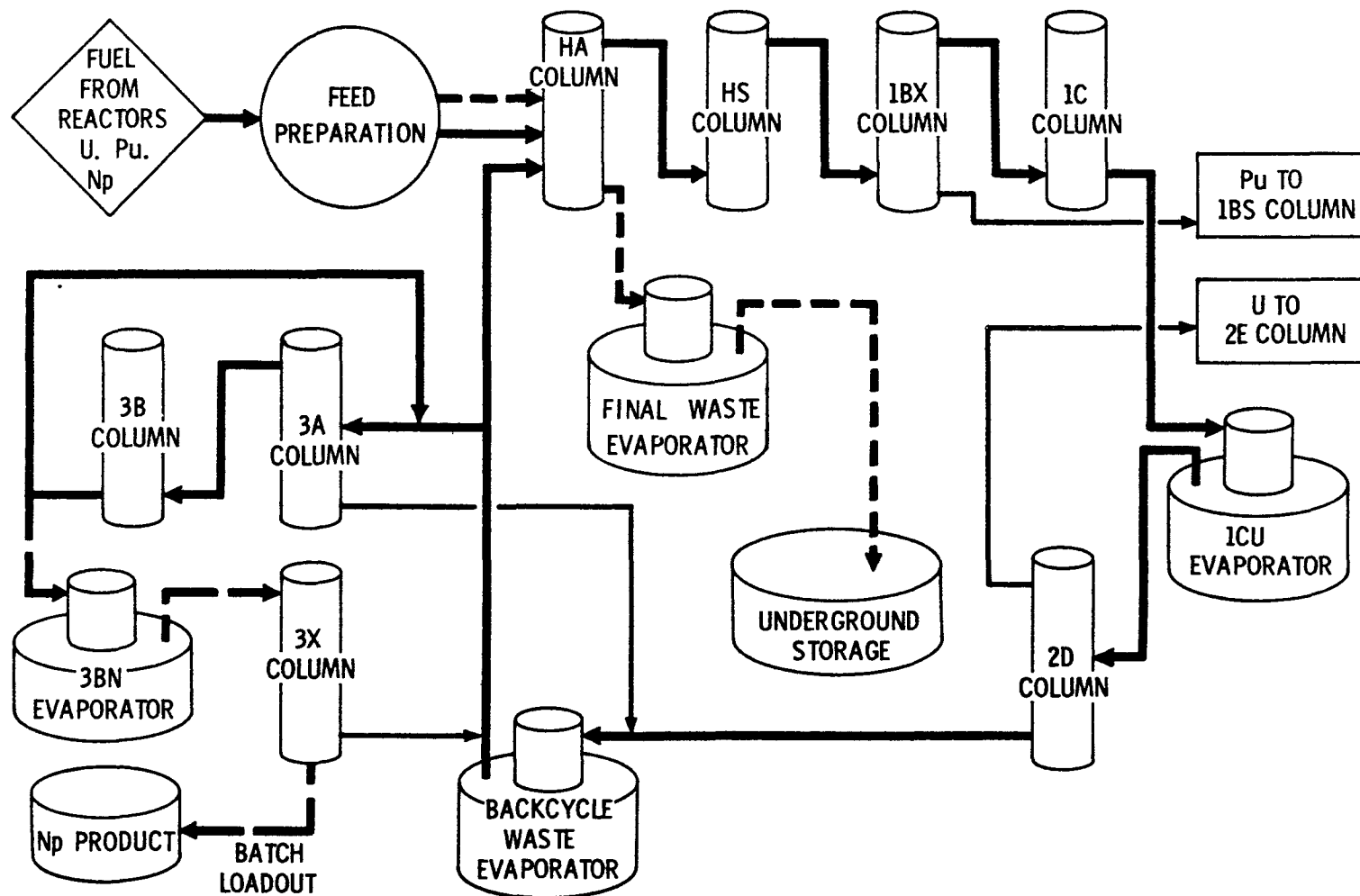


FIGURE 2

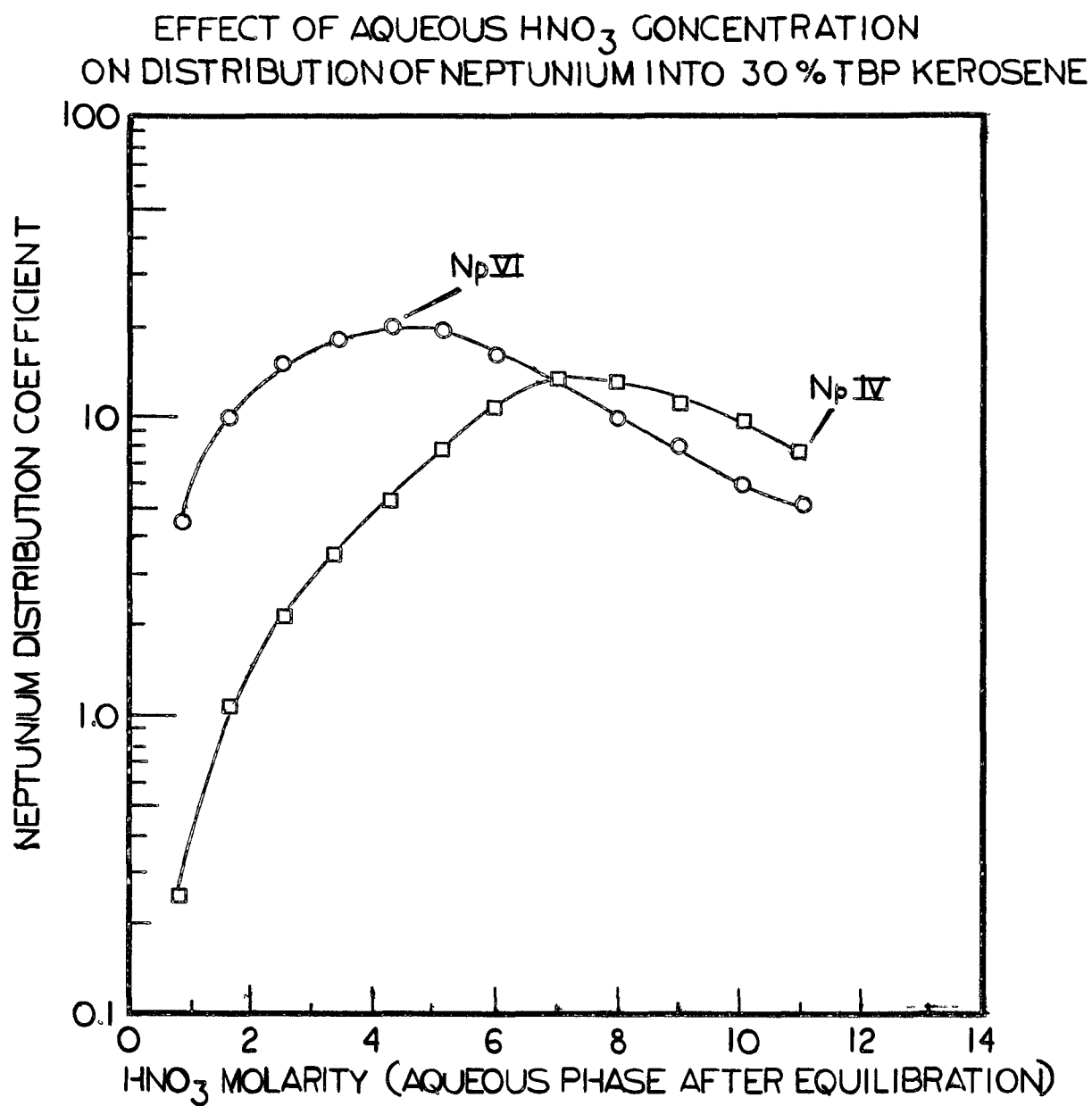


FIGURE 3

NEPTUNIUM RECOVERY AT PUREX

ACCUMULATION PHASE FLOWSHEET

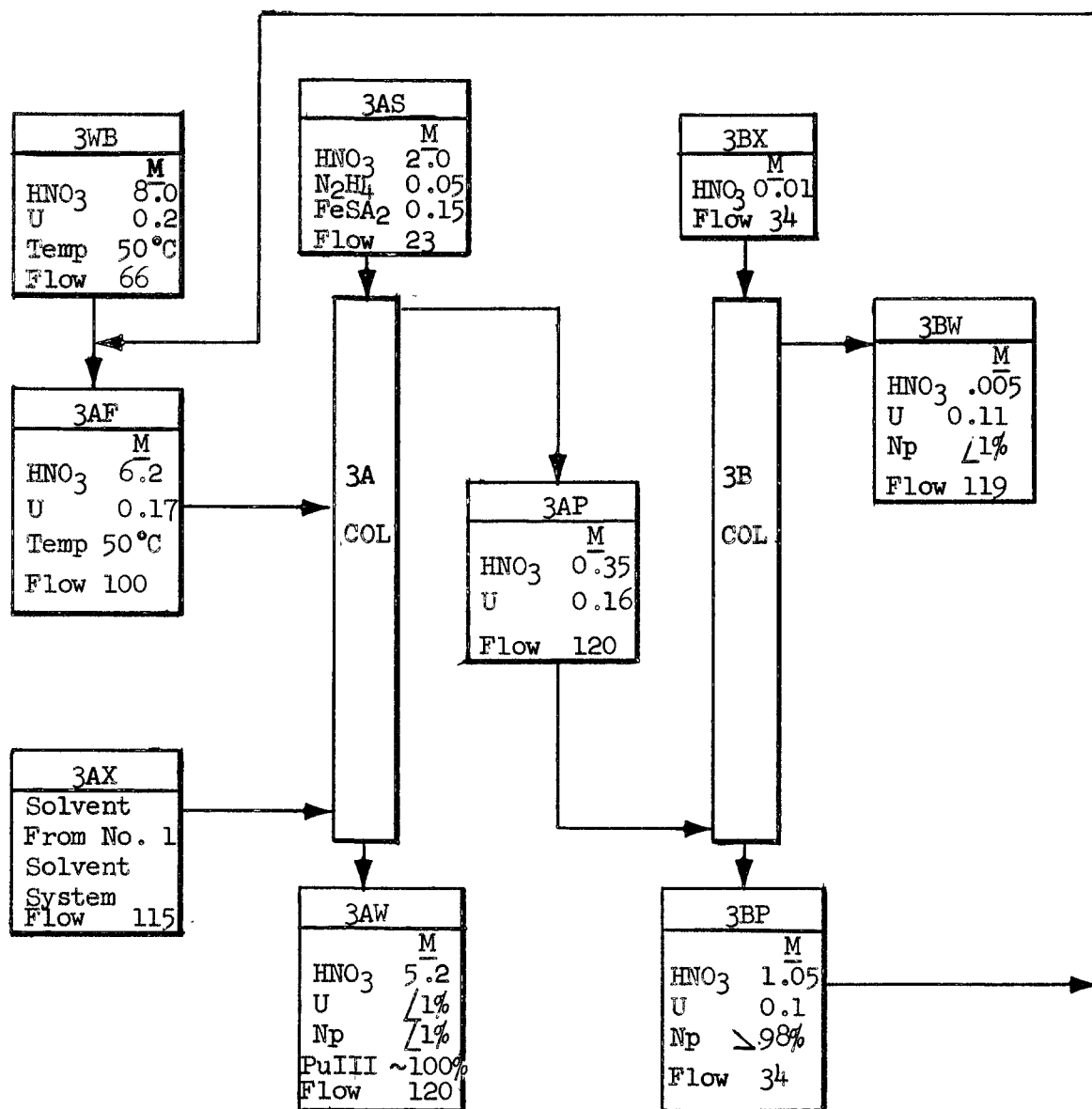


FIGURE 4

NEPTUNIUM RECOVERY AT PUREX
DECONTAMINATION PHASE FLOWSHEET

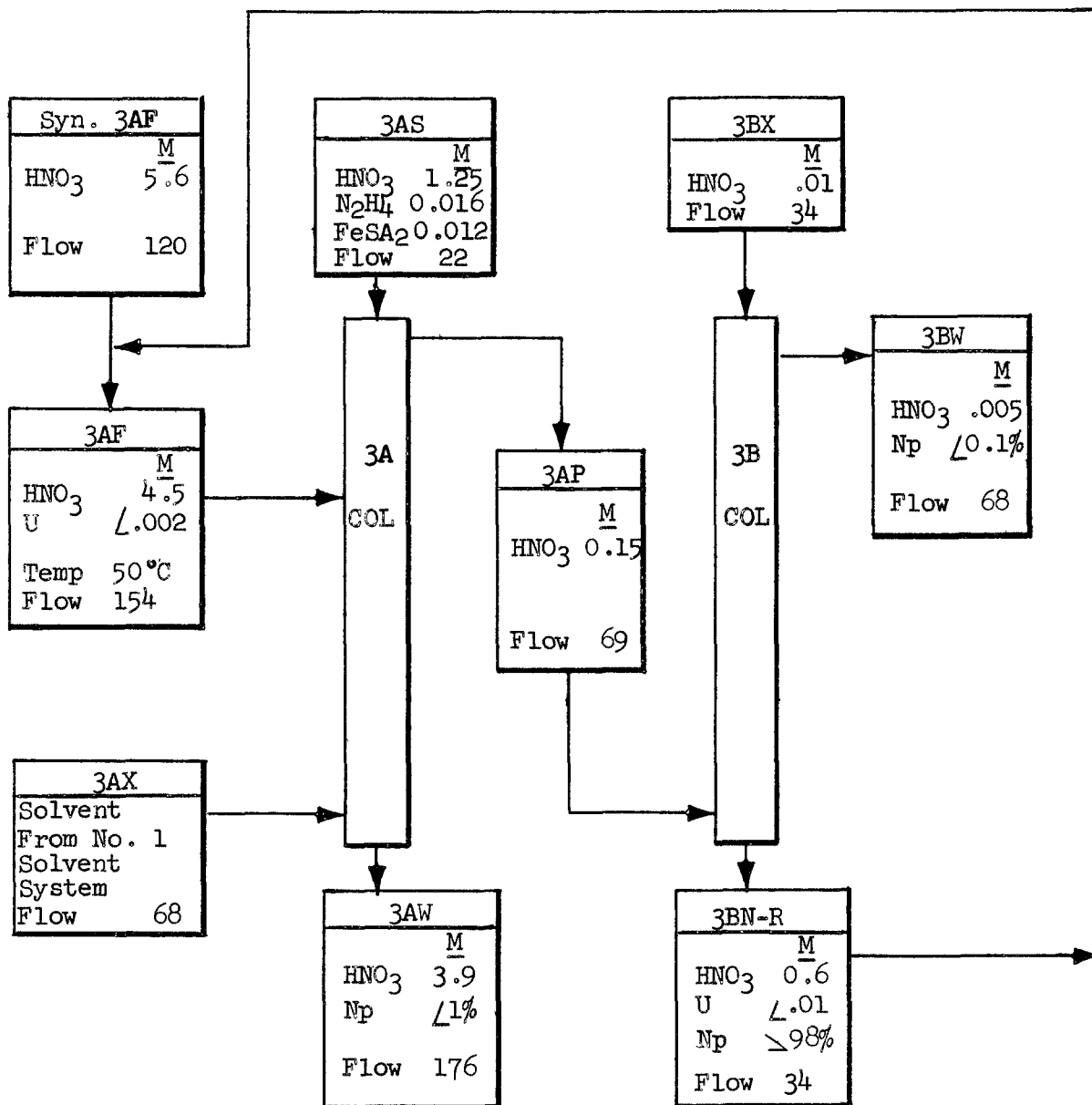
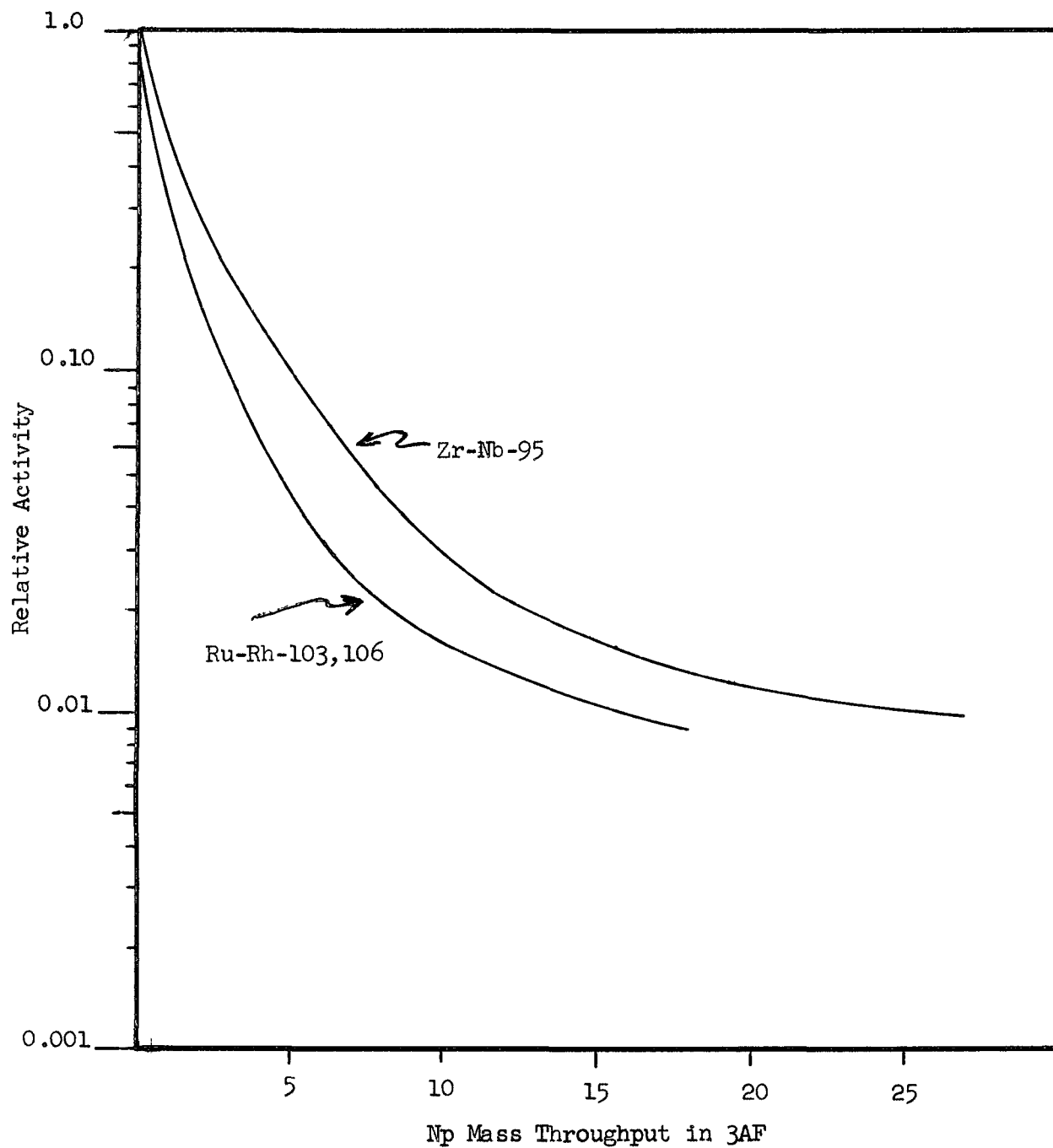


FIGURE 5

NEPTUNIUM RECOVERY AT PUREX

TYPICAL DECONTAMINATION PERFORMANCE



NEPTUNIUM RECOVERY FLOW DIAGRAM-BEFORE PROJECT CGC-913

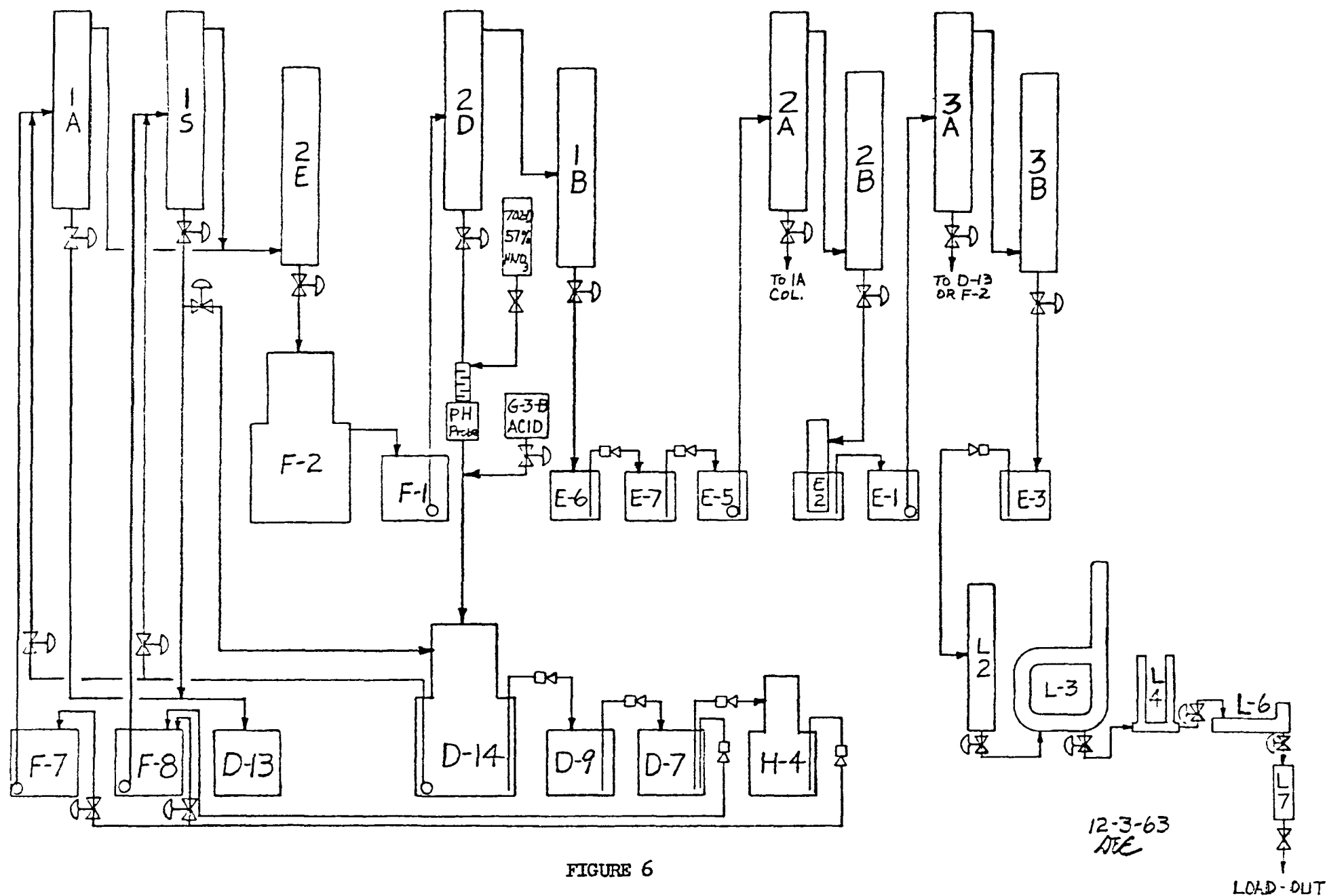


FIGURE 6

NEPTUNIUM RECOVERY FLOW DIAGRAM-AFTER PROJECT CGC-9/3

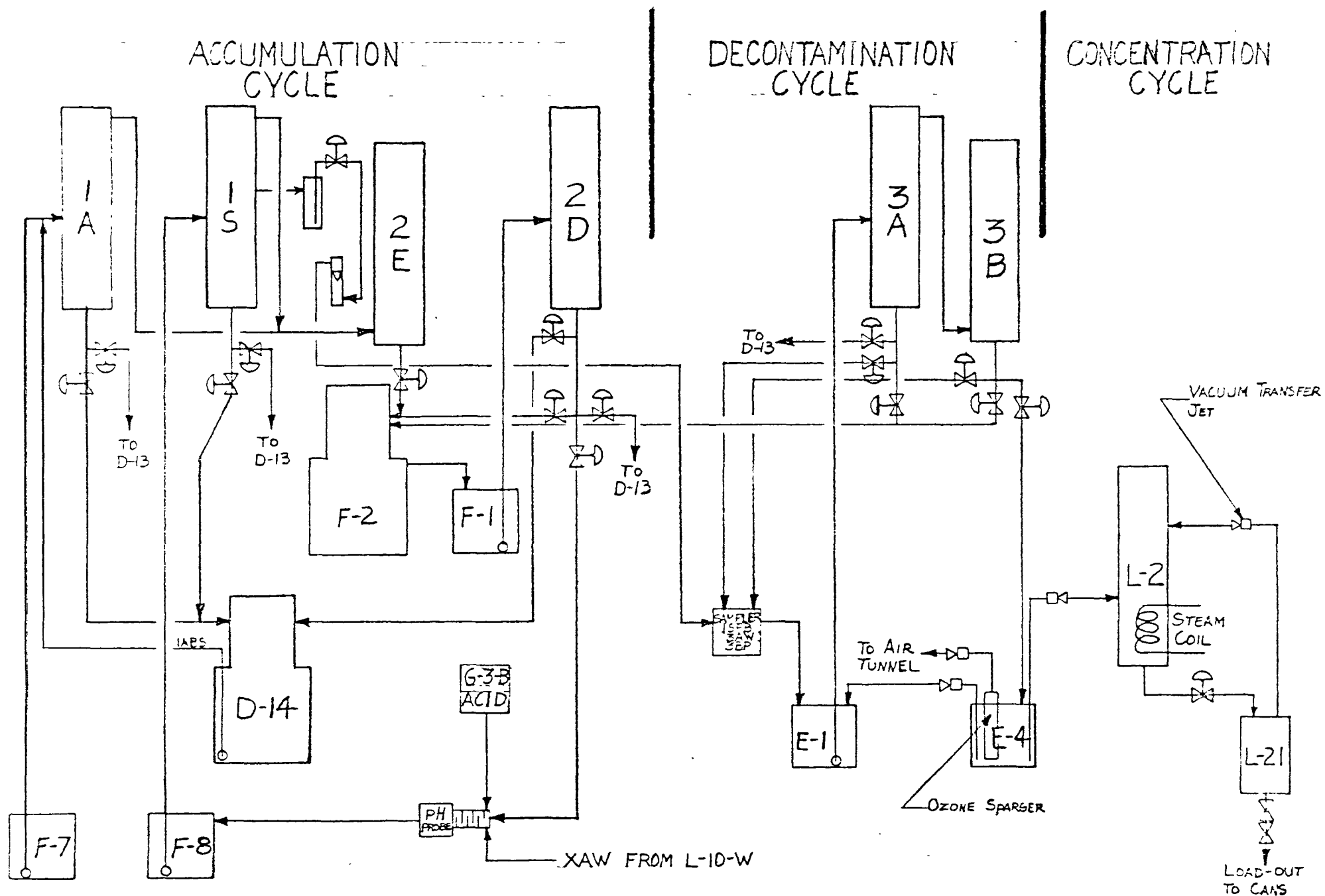


FIGURE 7

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FIGURE 8

EFFECT OF pH ON Np E_d^0 UNDER
REDOX EXTRACTION CONDITIONS

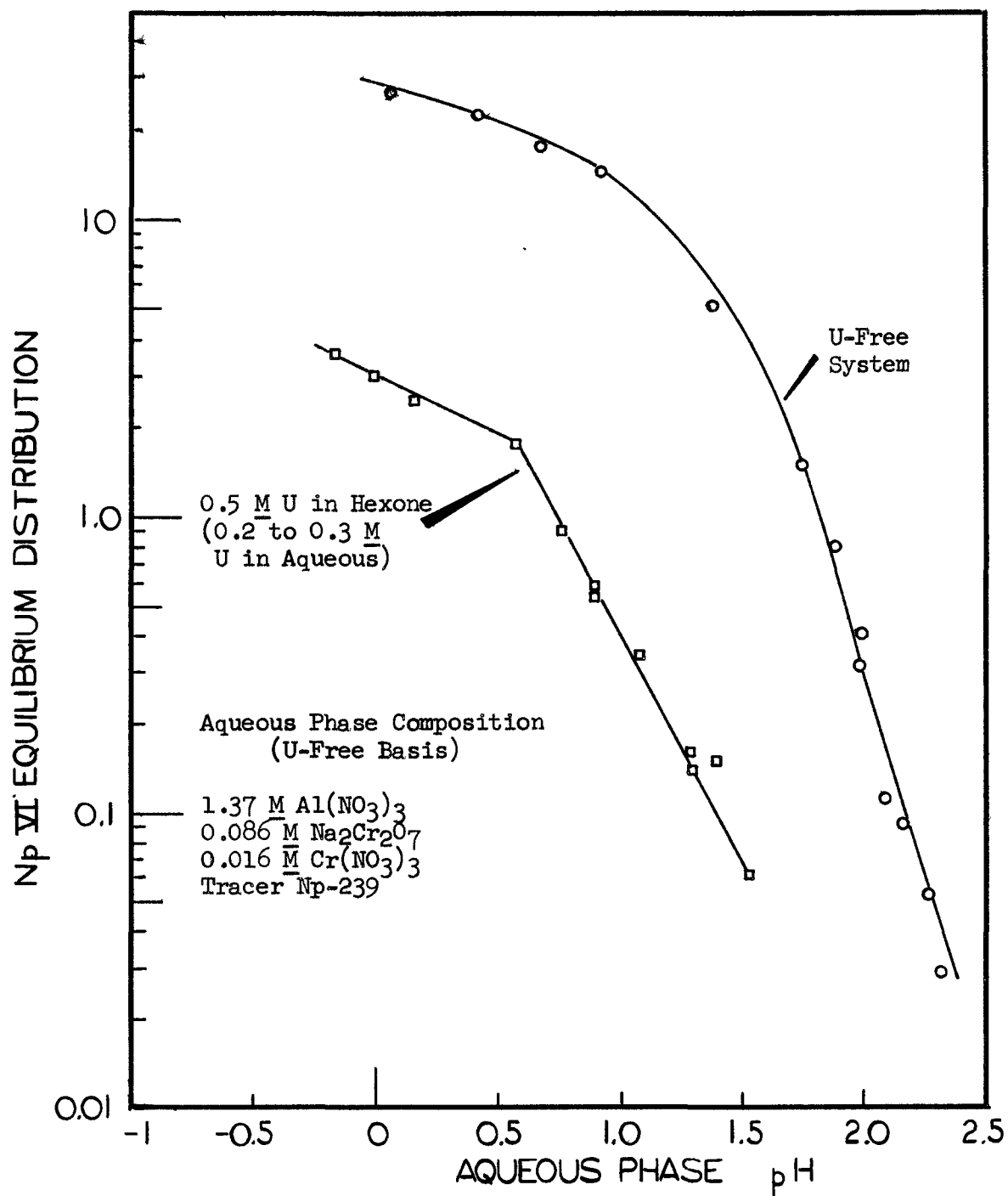


FIGURE 9

NEPTUNIUM PURIFICATION AT PUREX

BATCH ION EXCHANGE FLOWScheme

