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THE PUREX PROCESS - A SOLVENT EXTRACTION REPROCESSING METHOD FOR IRRADIATED URANIUM

E. R. IRISH and W. H. REAS

APRIL 8, 1957

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RICHLAND, WASHINGTON

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Chemistry-Separation Processes
for Plutonium and Uranium
(TID-4500, 13th Ed.)

1

THE PUREX PROCESS - A SOLVENT EXTRACTION REPROCESSING METHOD FOR IRRADIATED URANIUM *

By

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ABSTRACT

This paper describes the Purex Process, which employs solvent extraction to separate and purify uranium and plutonium from each other and from fission products contained in irradiated uranium fuel elements. A description of the over-all process, utilizing tri-butyl phosphate solvent (in a kerosene-type diluent) and nitric acid salting agent, is provided along with chemical process flowsheets. The process chemistry of uranium, plutonium, and fission products is discussed as affected by process variables. Methods of recovery of spent solvent and acid are briefly discussed. Alternate process arrangements are suggested.

THE PUREX PROCESS - A SOLVENT EXTRACTION REPROCESSING METHOD FOR IRRADIATED URANIUM

I. INTRODUCTION

The Purex Process is another continuous solvent extraction process which has been developed and demonstrated through laboratory and pilot plant work to recover and purify uranium and plutonium from irradiated uranium fuel. This process performs the same functions and has the same products as the Redox Process, but it differs in the use of solvent and salting agent. Whereas the Redox Process utilizes hexone, methyl isobutyl ketone, for a solvent and aluminum nitrate for a salting agent, The Purex Process utilizes tri-butyl phosphate as the solvent and nitric acid as the salting agent. Advantages of the Purex Process stem primarily from the following points: (1) the tri-butyl phosphate solvent system is safer as a result of the higher flash point and lower volatility of the solvent, and (2) the nitric acid salting agent is readily recoverable (by distillation), permitting much lower requirements for both waste storage and essential materials. Aside from these two differences, the two processes parallel each other considerably.

The tri-butyl phosphate, solvent extraction, fuel-processing system involves a maximum of six major steps:

1. Extraction of uranium and plutonium from aqueous solutions into the organic TBP-diluent phase.
2. Partitioning of the uranium and plutonium.
3. Decontamination and recovery of the uranium.
4. Decontamination and recovery of the plutonium.
5. Solvent recovery.
6. Nitric acid recovery (including waste concentration).

All six of these steps will be briefly discussed in this paper, along with an over-all chemical flowsheet, one of several which are feasible.

Preparation of the feed solution to the Purex Process was discussed in the previous paper. Solvent extraction contacters for carrying out the process will be discussed in the subsequent paper. Auxiliary processes (such as head-end treatment of feeds and tail-end treatments on product solutions) will be discussed in another session.

II. BASIC PROCESS PRINCIPLES

It is not within the scope of this paper to discuss comprehensively all the process chemistry of the Purex Process. Rather, it is the intent to present some highlights which will lend understanding of the process. Detailed comprehensive data must be derived from the development literature.

A. Solvent Action of TBP

The solvent action of tri-butyl phosphate depends on its complexing action. For example: uranyl nitrate reacts with TBP according to the reaction:

$$UO_2^{+2}(aq)+2\ NO_3^-(aq)+2\ TBP(org) \rightleftarrows UO_2(NO_3)_2 \cdot 2\ TBP(org).$$

If we define K_U as equal to the equilibrium constant for this reaction, we can write the useful relationship defining the distribution coefficient (i.e., the ratio of the concentration of uranium in the organic phase to that in the aqueous phase),

$$E^{o/a}_U = K_U \left(NO_3^-(aq)\right)^2 \left(TBP\ (org)\right)^2$$

where the (NO_3^-) concentration is the aqueous phase concentration and the TBP concentration is the uncomplexed TBP concentration in the organic phase. Since uranyl nitrate does not form a perfect solution in water under process conditions, K is not constant for the equilibrium expressed but varies somewhat with the concentration of the various solution components.

However, inspection of the equation provides a generally correct explanation of the nature and magnitude of the effects of the concentrations of uranyl nitrate, nitric acid, and TBP on the distribution ratio of uranyl nitrate. A similar analysis to that for uranyl nitrate may be applied for the solvent extraction of plutonium IV. However, the concentration of the plutonium itself may usually be neglected in the analysis since the plutonium concentration is almost invariably low enough for its self-salting and solvent-saturating effects to be insignificant. Thus, for plutonium IV:

$$E^{o/a}{}_{Pu} = K_{Pu} \left(NO_3^-(aq)\right)^4 \left(TBP(org)\right)^2.$$

Again the TBP concentration in the organic phase is the uncomplexed TBP concentration, and if uranium is also present, this fact must also be taken into account. These relationships show the effect of the nitrate ion concentration in the aqueous phase on the distribution coefficients. This effect is defined as the "salting" effect. Fortunately, the degree of TBP complexing of fission products is much less than that of uranium and plutonium; thus, a high degree of separation is possible.

B. Typical Distribution Coefficients

In Table I the relative order and magnitude of TBP extraction of uranium, plutonium, nitric acid, and the principal troublesome fission products contained in "aged" irradiated uranium are indicated:

TABLE I

Distribution Coefficients for Uranium, Plutonium and Fission Products for Extraction from Feed, 25 C.

ION	$E^{o/a}$
U(VI)	8.1
Pu(IV)	1.55
Pu(VI)	0.62
HNO_3	0.07

TABLE I (Contd.)

ION	$E^{o/a}$
Zr	0.02
Ru	0.01
Pu III	0.008
Nb	0.005
Rare Earths	0.002

Aqueous phase before equilibration: 3M HNO_3
200 grams U per liter
tracer level

Organic phase (30% TBP) after equilibration: 60% saturation

It is evident from this tabulation that uranium and plutonium IV are very extractable and that the fission products (zirconium, ruthenium, niobium, and rare earths) and plutonium III are quite inextractable. This characteristic difference between uranium and plutonium IV and the fission products permits the decontamination of uranium and plutonium. The extreme difference between the distribution coefficients for uranium and plutonium IV and that of plutonium III is the property which permits separation of uranium and plutonium from each other, and this will be discussed later.

Two terms in Table I need explanation. The TBP is diluted with a hydrocarbon diluent to 30 volume per cent in the Purex Process. This is done in order to give the solvent phase a low enough specific gravity (i.e. specific gravity of 0.841 at 25 C, which increases to 0.975 when the TBP is 85 per cent saturated) so that it can flow by gravity up through the contacting aqueous phase. (In the Halex Process, the TBP is diluted with carbon tetrachloride, and the aqueous phase flows upwards through the organic phase). The second term needing definition is "saturation" as applied to TBP. The TBP is considered to be 100 per cent saturated when all of it is complexed with uranium; for a 30 volume per cent TBP solution, a concentration of 124 grams uranium per liter represents complete saturation.

C. Variation of Distribution Coefficients with Nitric Acid

In Table II are tabulated some distribution coefficients for uranium, plutonium and fission products at varying nitric acid concentrations in order to illustrate the effect of variations in the nitrate salting strength on the distribution coefficients.

TABLE II

Variations in Distribution Coefficients as a Function of Aqueous HNO_3 Concentration

HNO_3 M	U	Pu IV	Ru	Zr	Nb	Rare Earths
0.5	1.18	0.10	0.0073	0.0007	0.0001	0.0004
2	2.84	0.46	0.0031	0.0031	0.0003	0.0005
3	3.28	0.59	0.0009	0.001	0.0004	0.0004
4	4.28	1.11	0.0005	0.024	0.0012	0.0004
5	4.16	1.55	0.0002	-	0.0018	0.0002
6	3.61	2.62	0.0002	0.089	0.0032	0.0001

Aqueous phase before equilibration: tracer level
200 grams U per liter

Organic phase (30% TBP) after equilibration: 80% saturation

It is evident from the data presented in this table that the uranium and plutonium distribution coefficients increase markedly as the nitrate salting effect increases, and zirconium and niobium follow in a similar manner, still sufficiently lower, however, to permit decontamination of the uranium and plutonium. However, the ruthenium distribution coefficients follow an inverse pattern. Thus, for optimum separation of the troublesome fission products from uranium and plutonium, a nitric acid concentration in the medium range (e.g., 2 to 3 M HNO_3) must be selected.

D. Variation of Distribution Coefficients with Saturation

In Table III are tabulated some distribution coefficients for uranium, plutonium, and fission products at varying uranium saturations of the solvent in order to illustrate the effect of the availability of uncomplexed TBP on the distribution coefficients.

TABLE III

Uranium Saturation of TBP, Per Cent	$E^{o/a}$ at 25 C				
	U	Pu IV	Ru	Zr	Rare Earths
28.0	16.7	4.0	0.067	0.041	0.0096
45.6	12.1	2.3	0.028	0.025	0.0048
61.7	7.9	1.6	0.0096	0.020	0.0021
72.0	5.4	1.1	0.0037	0.012	0.0011
82.4	3.6	0.79	0.0016	0.009	0.0004

Aqueous phase before equilibration: 3 $\underline{M}$ HNO_3
tracer level

Organic (30% TBP)-to-aqueous ratio: 2 to 1

As would be expected, the uranium distribution coefficient decreases as 100 per cent saturation is approached because of the lower concentration of uncomplexed TBP. The distribution coefficients for the other ions decrease in a similar manner.

E. Chemistry of Plutonium in Purex Process

Three chemical reactions of plutonium valence adjustment are important to permit quantitative plutonium recovery in the process and a high degree of separation of uranium and plutonium. The first reaction represents the reduction of hexavalent plutonium to tetravalent plutonium, the most extractable valence state:

$$PuO_2^{+2} + NO_2^- + 2H^+ \rightleftharpoons Pu^{+4} + NO_3^- + H_2O.$$

The nitrite ion can be added to the solution either as a salt (e.g., $NaNO_2$) or as a gas (e.g., NO_2), and the reaction is rapid, being essentially complete in a few minutes at 50 C.

The second reaction indicating the reduction of plutonium IV to plutonium III by ferrous ion is likewise almost instantaneous:

$$Pu^{+4} + Fe^{+2} + (NH_2SO_3^-) \rightleftharpoons Pu^{+3} + Fe^{+3} + (NH_2SO_3^-).$$

Ferrous ion (added as ferrous sulfamate) is used as the reductant, with the sulfamate ion acting as a nitrite suppressor. If the sulfamate ion were not present, low concentrations of nitrite ion (always found in nitrate systems in the absence of sulfamate or some similar ion) would initiate the autocatalytic oxidation of the ferrous ion, thus preventing plutonium reduction. A several-fold excess of ferrous sulfamate is used to assure a reducing solution. When reoxidation of the plutonium is again desired, the reaction indicated by the third equation is initiated, again using the nitrite ion but this time as an oxidant:

$$2NH_2SO_3^- + 2NO_2^- \longrightarrow 2N_2 + 2SO_4^{-2} + 2H_2O \text{ followed by}$$

$$6Pu^{+3} + 2NO_2^- + 8H^+ \longrightarrow 6\,Pu^{+4} + N_2 + 4H_2O.$$

The nitrite ion is an ideal oxidizing agent because of its ability to oxidize plutonium only to the tetravalent state, the most extractable form for further processing. You will note that sulfate ion is formed, and if excessive amounts of sulfate ion are formed, plutonium sulfate is formed which is inextractable during subsequent solvent extraction processing. Thus, the chemical flowsheet must be defined to minimize formation of this complex.

One other characteristic of tetravalent plutonium should be mentioned. In low acidities, dependent upon the plutonium concentration and total nitrate concentrations, an inextractable polymeric species of plutonium may form.

A. Co-Decontamination Cycle Flowsheet, HA Column

In Figure 1 the HA Column accomplishes the primary separation of the highly radioactive feed solution into an organic product stream and a first-cycle aqueous waste stream containing greater than 99.9 per cent of the fission products. The feed solution (HAF) from the dissolvers and feed preparation equipment is fed continuously to the midpoint of the HA Column and flows downward into the extraction section countercurrent to an upward flow of organic extractant (HAX). Conditions of flow and salting strength are regulated in such a manner that the uranium VI and the plutonium IV are coextracted almost quantitatively into the organic phase, leaving most of the fission products and other impurities in the aqueous phase. Some fission products are extracted, however, by the solvent at the feed point and in the lower portion of the column, but these are partially backwashed or "scrubbed" into an aqueous nitric acid scrub stream (HAS) flowing countercurrent to the product-bearing solvent stream in the upper (scrub) section of the compound column. The bulk of the impurities and nitric acid leave the bottom of the column in the aqueous effluent stream (HAW) which is sent to acid recovery. The acid recovery flowsheet will be discussed later. The product bearing stream (HAP) is cascaded from the top of the HA Column to the bottom of the HC Column.

HC Column

The HAP enters the bottom of the HC Column and is contacted by a countercurrent flow of aqueous strip solution (HCX). The uranium and plutonium are stripped back into the aqueous phase. A trace of nitric acid is added to the HCX stream to decrease the susceptibility of the HC system to emulsification. The product-free organic (HCW) is sent to solvent treatment (also to be described later), and the aqueous-effluent (HCP) containing the uranium and plutonium is steam-stripped of residual dissolved and entrained organic phase, then concentrated to meet Partition Cycle feed specifications. After one complete cycle the products are generally decontaminated from the gross fission products by a factor of 10^3 to 10^4, and additional decontamination may be needed to meet the product-purity requirements. Product recoveries may approximate 99.9 per cent.

B. Partition Cycle (Figure 2) 1A Column

The product-bearing stream overflows from the Co-Decontamination Cycle concentrator into the 1A Column feed preparation section where any plutonium (VI) formed within the concentrator is stabilized as plutonium (IV) by reduction with sodium nitrite. Ruthenium and zirconium-niobium are the principal remaining fission products in the 1A Column feed (1 AF). The 1 AF is pumped continuously to the mid-point of the 1A Column. The 1A Column is operated as a decontamination column in a manner analogous to that described previously for the HA Column. The organic-product stream (1AP) overflows the 1A Column and is combined with the organic effluent of the 1B Scrub Column (to be described later) to form IBXF.

IBX Column

The combined organic effluent of the 1A and 1BS Columns (IBXF) is pumped to the bottom of the IB Extraction (IBX) Column. As the organic rises through the IBX Column, it is contacted with a countercurrent flow of slightly acidified ferrous sulfamate solution (IBX). Ferrous iron in the aqueous phase reduces the plutonium from valence IV to valence III, which is only weakly complexed by the solvent, thus permitting the plutonium (III) to be extracted into the aqueous phase. Some uranium also tends to strip out of the solvent into the aqueous phase, but the majority is held in the organic by the high salting strength of nitric acid refluxed within the column. The aqueous effluent from the IBX Column (IBXP) containing the plutonium and approximately one per cent of the uranium is fed to the top of the IBS Column. The organic effluent (IBU containing the uranium cascades to the IC Column).

IBS Column

The uranium present in the IBXP is stripped by contacting with fresh 30 per cent TBP (IBS) in the IBS Column. The uranium-bearing organic stream (IBSU) overflows the IBS Column and is routed to combine with the IAP to form the IBXF stream, previously described. The plutonium bearing stream (IBP) leaves the bottom of the IBS Column and passes to the Final Plutonium Cycle.

After two complete cycles the plutonium is decontaminated from gross fission products by a factor up to 5×10^5, and additional decontamination may be generally required to meet product-purity requirements. Partition Cycle plutonium decontamination factors are typically 20 to 50. Product recoveries in the range of 99.9 per cent may be accomplished.

IC Column

The uranium bearing stream (IBU) overflows the IBX Column and flows into the bottom of the IC Column. The uranium is transferred into the aqueous phase in the IC Column by countercurrent extraction in a manner comparable to that of the HC Column. The product-free solvent (ICW) is sent to solvent recovery. The aqueous effluent (ICU) is steam-stripped of residual organic phase, and concentrated in the ICU concentrator to meet Final Uranium Cycle feed specifications.

After two complete cycles the uranium is decontaminated from gross fission products by a factor up to 1×10^6, and additional decontamination may be required to meet product purity requirements. Partition Cycle uranium decontamination factors are typically 50 to 100. Uranium recoveries may approximate 99.9 per cent.

C. Final Uranium Cycle (Figure 3) Feed Preparation

The Final Uranium Cycle completes the removal of fission products and plutonium from the uranium to permit direct handling of the uranium product. Of the fission products originally present, on the order of 0.01 per cent remain in the feed, along with a small amount of plutonium. Zirconium, niobium, and ruthenium remain as the principal fission product contaminants, although the ratio of ruthenium to zirconium-niobium will vary considerably in different flowsheet variations.

of hydrolysis products of TBP, namely dibutyl phosphate (DBP), monobutyl phosphate (MBP), and phosphoric acid, primarily DBP. Both the DBP and MBP have a marked effect on plutonium behavior in the Purex Process, the DBP for its strong complexing of plutonium IV and the MBP for its tendency to form a precipitate with plutonium IV. Both DBP and MBP form weak complexes with plutonium III and neither affects the plutonium III distribution ratio appreciably. However, owing to the complexing action of DBP on plutonium IV, plutonium IV losses during stripping become excessive unless the DBP concentration of the solvent is kept below 0. 001 per cent. Similar behavior exists with uranium also. Because both MBP and DBP are acidic in nature, they are readily removed from the used solvent with the dilute sodium carbonate wash. Dilute caustic is also satisfactory for DBP and MBP removal, but it will precipitate uranium and plutonium whereas sodium carbonate forms soluble complexes of these metallic ions.

The carbonate wash also is used to remove residual uranium, plutonium, and fission products (primarily ruthenium, zirconium, and niobium) from the solvent before recycle. With this simple washing procedure, solvent quality is maintained at a satisfactory quality for continued recycle.

Process degradation of the diluent, a kerosene-type hydrocarbon, under normal conditions is not a serious problem. However, the hydrocarbon selected should be one of high purity, low in unsaturated compounds and preferably non-cyclic in nature for maximum stability to radiation and chemical degradation. A diluent having a high flash point is desirable to minimize safety hazards. The sodium carbonate wash has essentially no beneficial effect on diluent quality and continued development work is in progress to determine the most satisfactory commercial diluents and to devise chemical means for overcoming process degradation of diluents.

F. Nitric Acid Recovery (Figure 6)

The nitric acid recovery flowsheet illustrated (Figure 9) consists of a two-stage distillation and absorption and fractionation. The economic incentive for acid recovery from extraction wastes is based primarily on savings of waste storage space, with relatively minor savings resulting from the decrease in nitric acid and sodium hydroxide (for neutralization) consumption. In properly sized equipment, the degree of acid recovery is limited only by the maximum allowable concentration factor which is permitted before the formation of excessive solids (from sodium nitrite and ferrous sulfamate). You will note in the flowsheet that the first-cycle waste acid (HAW) is recovered by a double distillation (to permit adequate decontamination of the recovered acid) whereas the other acid waste is only distilled once prior to absorption and fractionation. The degree of acid recovery is controlled by adjusting the feed and concentrate acidities so that the feed acidity is approximately equal to the vapor concentration in equilibrium with the concentrate. In this manner the majority (85-95 per cent) of the acid is distilled and then can be fractionated to 50 to 60 weight per cent nitric acid by conventional means. The high-activity acid concentrate (6 to 10 M HNO_3) is neutralized and sent to underground storage where further self-concentration (from the heat of fission product decay) can be achieved. This concept will be discussed in more detail in a later session.

Decontamination factors across a double-distillation system (gross gamma DF on the order of 1×10^6 to 10^7) are sufficient to allow use of the recovered nitric acid in all process streams except the final-cycle scrub streams. Ruthenium volatilization may become excessive at high (8 to 10 M) nitric acid concentrations, but this volatilization may be suppressed by the presence of low concentrations (ca 0.03 M) of nitrite ion, either added directly or formed by the reaction of entrained diluent with nitric acid.

An alternate to the flowsheet shown would be to route the 2WW acid concentrate to the HAF rather than to the IWF for disposal. By utilizing this alternate, the small quantities of uranium and plutonium contained therein can be recovered instead of discarded. If this alternate is used, TBP must be prevented from entering the waste system, since excessive hydrolysis products of TBP (DBP and MBP) could be recycled and result in high plutonium and uranium losses from the HC Column in addition to lowering the decontamination factor obtained in the HA Column.

A second reason for preventing the accumulation of TBP in the acid concentrator is related to chemical safety. TBP will form complexes with nitric acid (and also uranyl nitrate) which, if concentrated to a high degree, can result in an exothermic decomposition reaction of explosive violence. Purex Process conditions do not approach those required for such reaction. However, for process safety the product and acid concentrators should be protected to prevent such conditions from arising accidentally. Protection is readily possible since the reactions will not take place at atmospheric pressure until the mixture reaches 135 C for uranyl nitrate-TBP complexes and 150 C for nitric acid-TBP complexes. Limiting the maximum temperature of the sytem provides an adequate safeguard.

IV. ALTERNATE PROCESS ARRANGEMENTS

As mentioned earlier the flowsheet and flow patterns just discussed (Alternate A in Table IV) are only one variation of several satisfactory arrangements of the Purex Process. Other satisfactory chemical flowsheets with alternate A (i.e., three-cycle decontamination) can also be demonstrated, utilizing variations in the acidities of different feed solutions, different flow ratios, concentrations of TBP, etc. However, even more versatility of the Purex Process can be achieved by utilizing various head-end

TABLE IV

Alternate Purex Process Arrangements

	Head-End Treatments	Solvent Extraction Cycles		Tail-End Treatments	
		U	Pu	U	Pu
A	-	3	3	-	-
B	x	2	2	x	x
C	-	2	2	x	x
D	-	2	2	-	-
E	x	1	1	x	x

ACID RECOVERY

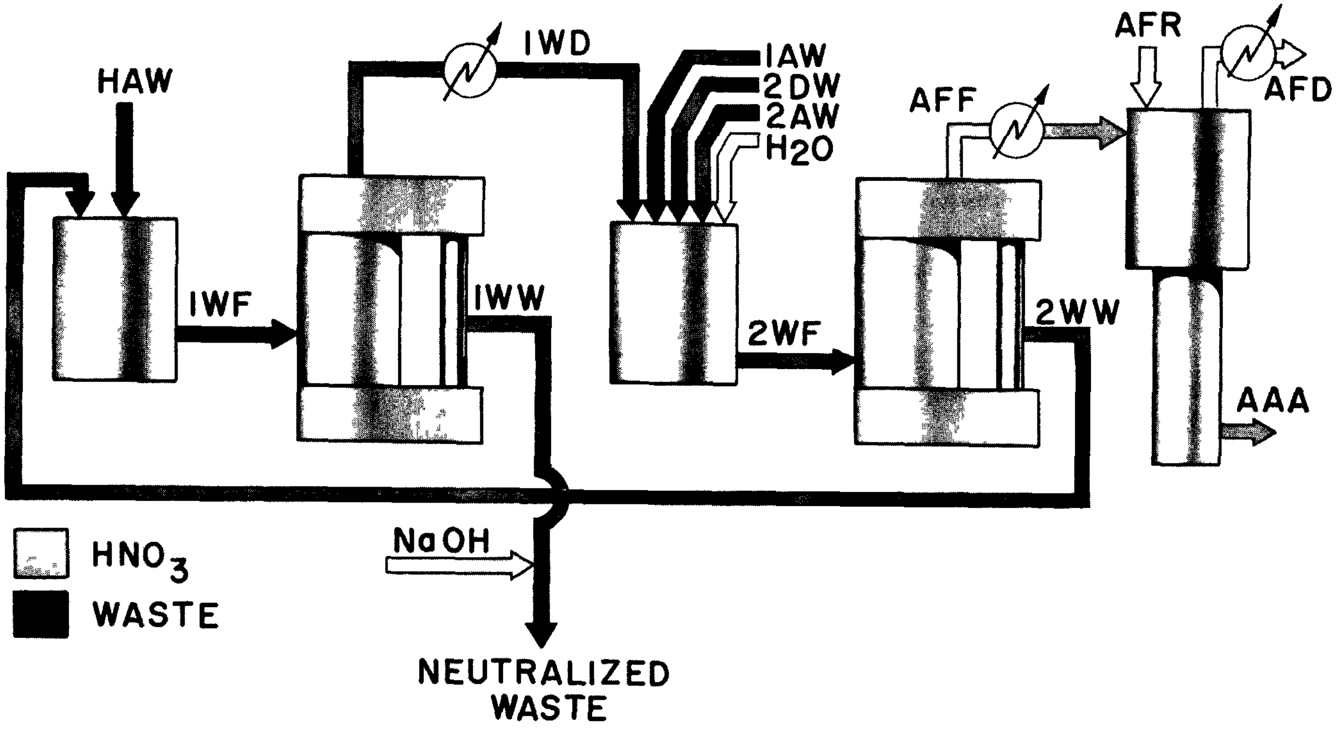

FIGURE 6

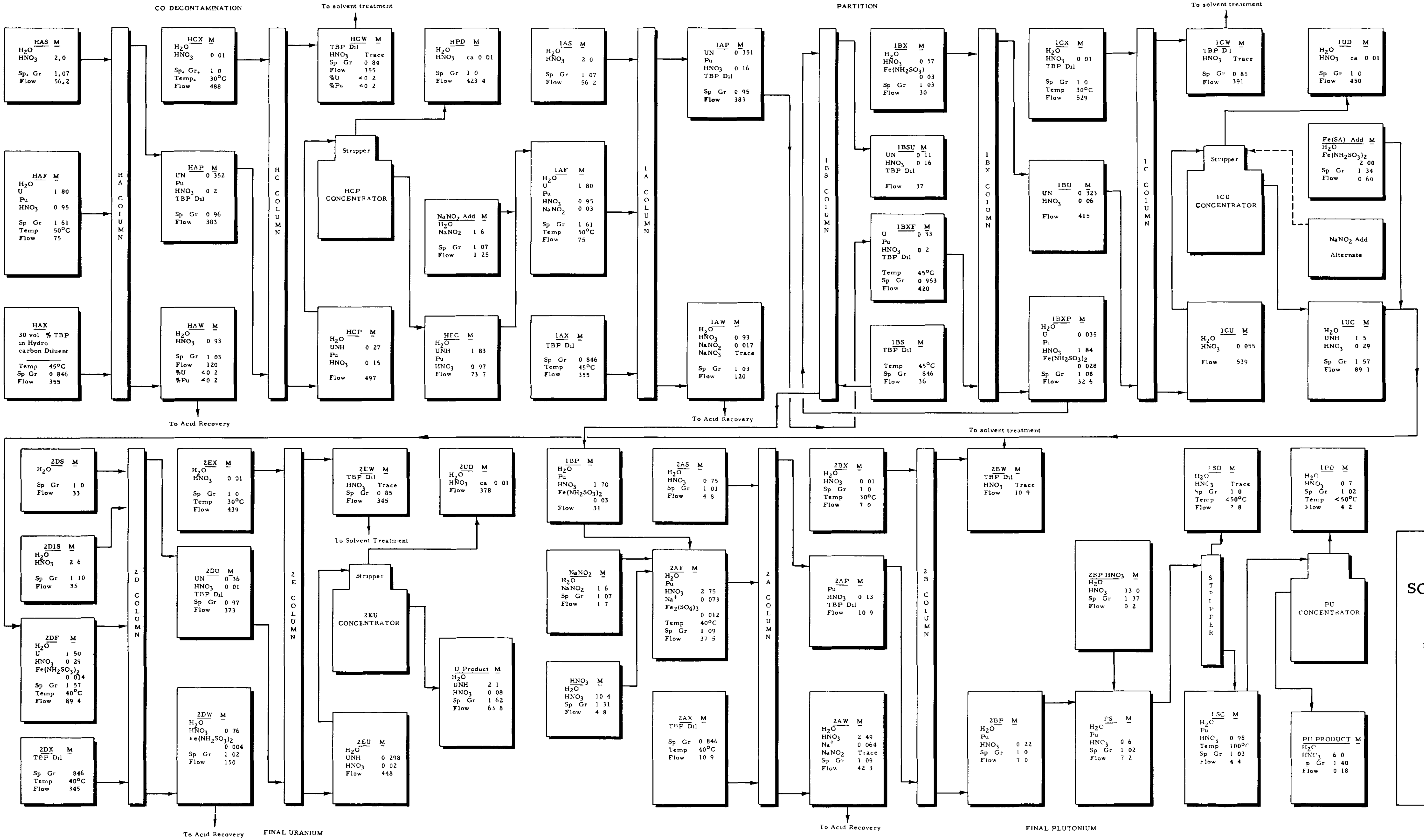

FIGURE 7
PUREX
SOLVENT EXTRACTION
FLOW SHEET

NOTES
1 100 FLOWS EQUALS 747 GALLONS OF SOLUTION PER TON OF URANIUM PROCESSED
2 ALL TEMPERATURES ARE AMBIENT UNLESS OTHERWISE SPECIFIED
3 SPECIFIC GRAVITIES OF ORGANIC SOLUTIONS ARE BASED ON A HYDROCARBON DILUENT WITH A SP GR OF 0 785

33

34

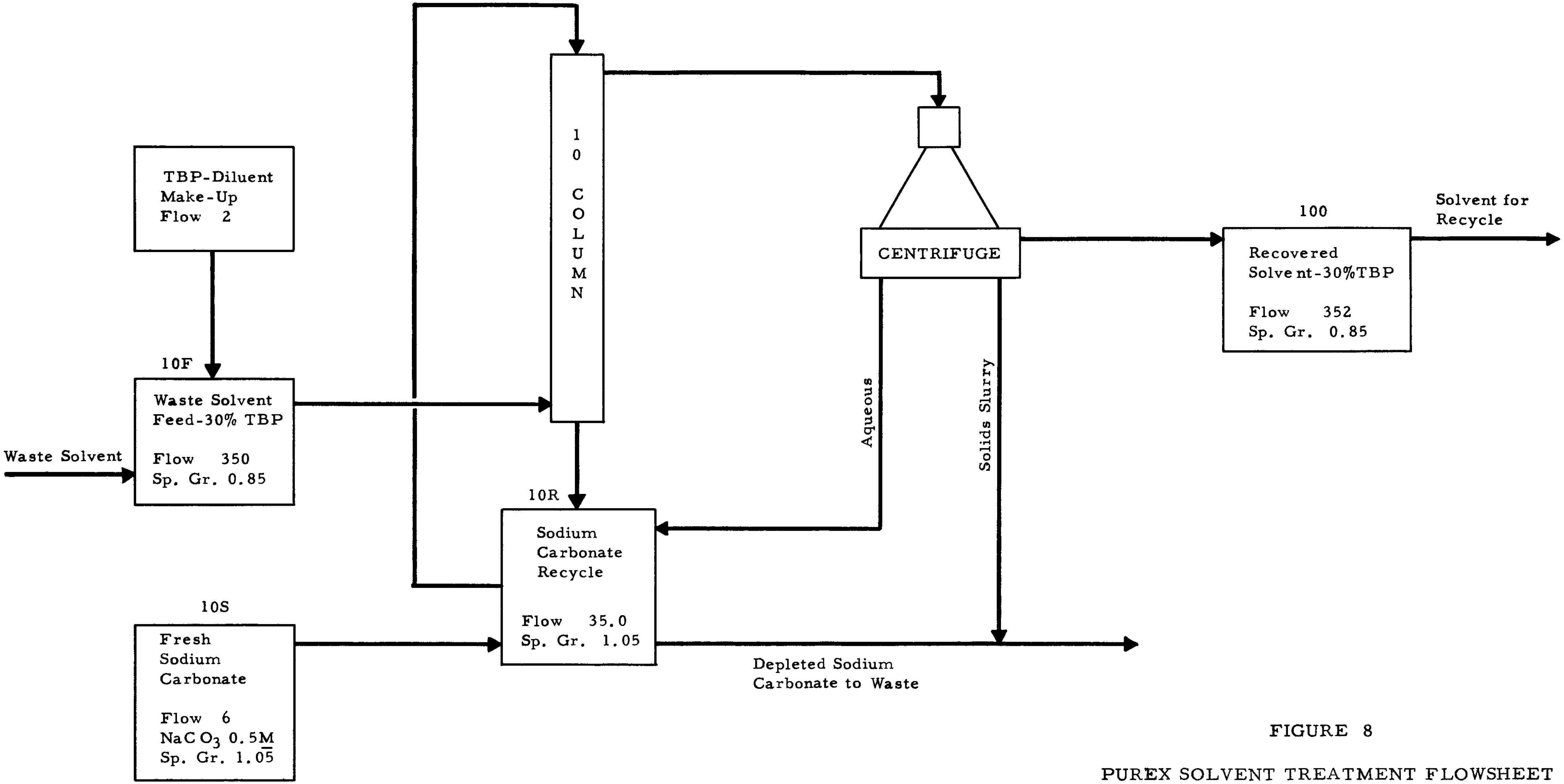

FIGURE 8

PUREX SOLVENT TREATMENT FLOWSHEET

(Based on Figure 7 Flowsheet)

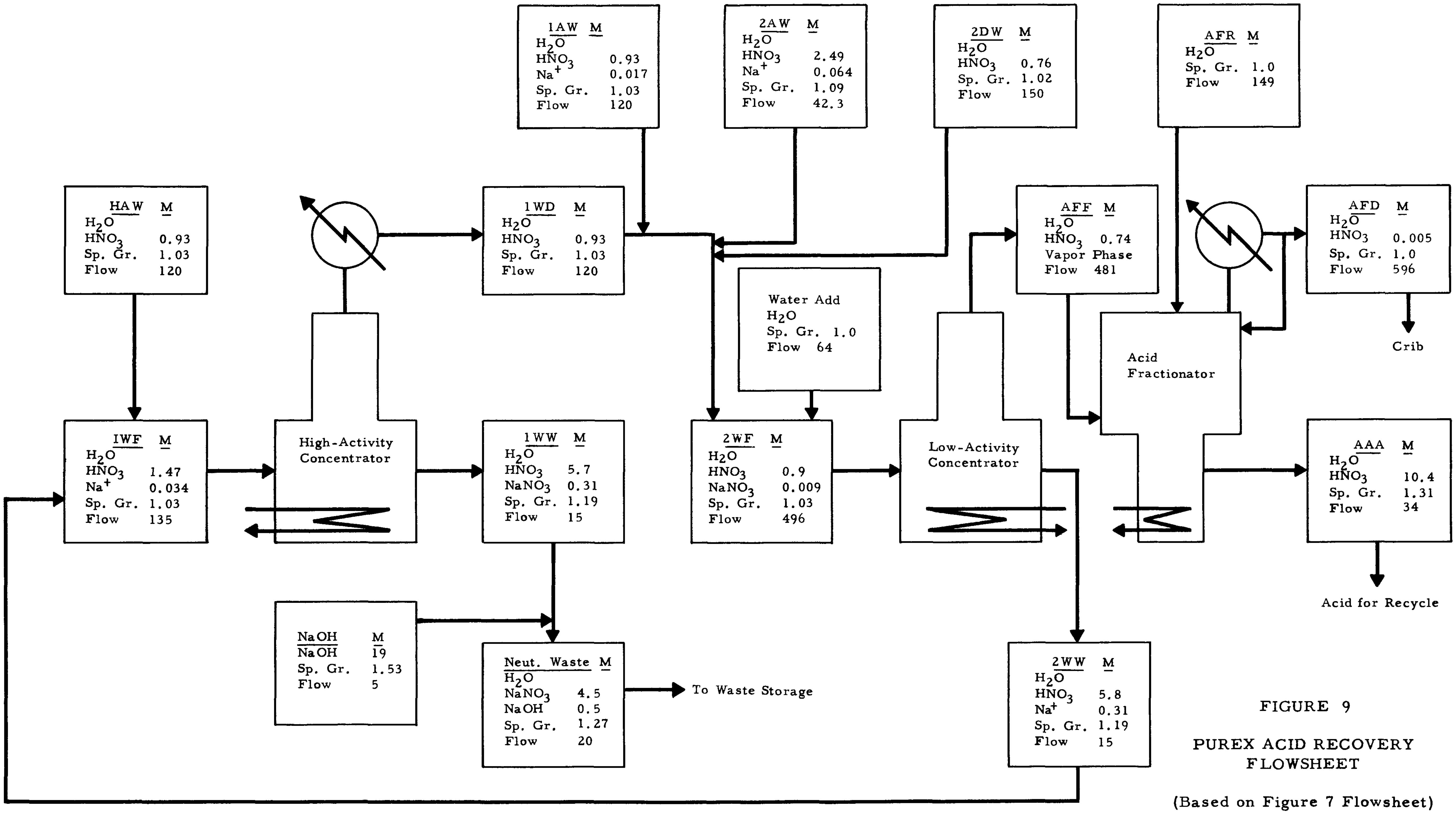

FIGURE 9

PUREX ACID RECOVERY FLOWSHEET

(Based on Figure 7 Flowsheet)