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CHEMISTRY SEPARATION PROCESSES FOR PLUTONIUM AND URANIUM

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TBP PROCESS FOR URANIUM RECOVERY FROM METAL WASTE-LABORATORY SUMMARY

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TBP PROCESS FOR URANIUM RECOVERY FROM METAL WASTE-LABORATORY SUMMARY

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1.0 Abstract

This report presents the progress in the laboratory development of the tributyl phosphate solvent extraction process for the recovery of uranium from metal waste. Methods of feed preparation, solvent specifications and cleanup procedures, plutonium studies, and tentative flowsheets are discussed.

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2.0 Introduction

A solvent extraction procedure employing tributyl phosphate as the solvent and nitric acid as a salting agent, was successfully demonstrated on a laboratory and Semi-Works scale at ORNL (see ORNL-260)[4] for the recovery of uranium from radioactive waste. For reasons previously reported (mechanical operability, ease of stripping), an inert diluent such as hexane was used in conjunction with the TBP.

Further laboratory development on this process was necessary (1) to develop a more satisfactory diluent for tributyl phosphate (i.e., "Varsol" or "Gulf BT" instead of hexane), (2) to determine alternate methods of feed preparation and solvent cleanup procedures, and, (3) to establish the behavior of plutonium under the conditions of the process.

Tributyl phosphate has been shown to complex uranium according to the following reaction:

$$UO_2^{++} + 2\ NO_3^- + 2\ TBP = UO_2(NO_3)_2\ TBP_2$$

for which the equilibrium expression can be used:

$$K = \frac{(UO_2)(NO_3)_2(TBP)_2\ \gamma_o}{(UO_2^{++})(NO_3^-)^2(TBP)^2\ \gamma^3 \pm UO_2(NO_3)_2}$$

Assuming the activity coefficients for the solvent species close to unity and inserting the values of $\gamma \pm$ for $UO_2(NO_3)_2$ [1] very good agreement of the data is obtained with a K value of 118. A very close approximation of the data is obtained by omitting the activity coefficients entirely, for which

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Introduction (continued)

a value for K_m is about 22, using "Varsol" as the diluent.

Although the reactions are not completely understood similar equations may be written for Pu^{IV}, Pu^{VI}, HNO_3 and most of the fission products. Both Pu^{IV} and Zr have an extractability only slightly less than U^{VI}. However, separation of uranium from the other contaminants can be accomplished by adjusting conditions such that, at the feed plate, the solvent is always near saturation in uranium (greater than 70%).

The present report largely concludes the laboratory investigation of the TBP process as applied to Hanford waste. The principle problems remaining consist of (1) establishing a method for the removal of the waste from the tanks, (2) scale-up of equipment to plant size using cold material (3) investigation of methods for ultimate disposal of the wastes after the removal of uranium.

The future laboratory program at ORNL will be devoted largely to the final development of an adequate TBP process for the recovery of uranium from the ORNL wastes.

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3.0 Summary

In laboratory countercurrent batch studies, decontamination factors of $1x10^{4}$, and uranium losses of less than 0.2% were demonstrated for the tributyl phosphate extraction of uranium from metal wastes. The operability of the process was satisfactorily demonstrated with feed solutions containing 0.1-0.6 M uranium (20-140 g/l), 0-1.3 M sulfates, and 0-0.7 M phosphates.

Acidified Hanford waste supernatant, to which was added the necessary ionic constituents to simulate total waste, was used as feed solutions in these experiments.

In all cases, the recovered uranium contained less than 20% of the beta activity of natural uranium and only background gamma activity.

It was also shown that the plutonium to uranium ratio in the product could be reduced to ca. $1x10^{-8}$ by using 0.05 M ferrous sulfamate in the scrub stream. However, scouting studies have indicated that, by eliminating the scrub section entirely, as much as 80-90% of the plutonium may be extracted with the uranium, and subsequently separated and recovered by stripping with ferrous sulfamate. The uranium remains in the organic phase and is stripped with water in a third column. For old wastes, this procedure would not appreciably alter the decontamination from fission product activity.

Other points of interest investigated include methods of feed preparation, solvent specifications, cleanup procedures, analytical methods, and variables affecting plutonium extraction.

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4.0 Feed Preparation

The most feasible method of feed preparation for use in conjunction with the TBP waste metal recovery process is probably that proposed for the UAP process, i.e., direct acidification of the total waste in conjunction with a slight amount of evaporation. This procedure would result in a feed three molar in nitric acid and containing 50 to 60 g/l of uranium. Scouting studies have indicated that even higher uranium concentrations may be feasible by proper adjustment of the acid concentration (ca. 2.0 M) before evaporation. The optimum solubility of the different salts occurs at 4-5.M HNO_3. Phosphates are not soluble at lower acid concentrations and nitrates are "salted out" by higher acid concentrations. The cost of chemicals for this feed preparation procedure amounts to about 48 cents per kilogram of uranium processed. This cost is considerably higher than for other methods subsequently considered, but has the advantages of simplicity of operation, no uranium losses, and no added solids to the waste streams (provided it is feasible to recover the waste HNO_3).

Although the above procedure is generally accepted as a desirable method of feed preparation, at present considerable uncertainty exists as to the means of removing the waste from the Hanford tanks. While most of the sludge may be removed by slurrying it with the accompanying supernatant to yield a slurry of "total waste", it is probable that some of the

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Feed Preparation (continued)

sludge can only be removed as a very dilute slurry by some form of hydraulic mining technique. Another possibility exists also that at some point it may become desirable to process the supernatant rapidly and separately from the sludge. To meet these exigencies, and to permit the evaluation of process costs at feed through-puts of higher uranium concentration, a number of alternate feed preparation steps have been evaluated on the basis of uranium loss, chemical costs, and operability (see Table 4.0-1).

Two simple precipitation procedures are available for concentrating uranium in waste solutions or slurries to approximately 100 - 140 g/l. Since the Hanford wastes are at present in a NaOH-carbonate complexed solution, addition of acid (either HNO_3 or H_2SO_4) to the bicarbonate end point (pH $\sim$ 4.4) results in a quantitative precipitation of the mixed phosphates and uranates of uranium. The uranium precipitate from either supernatant or total waste settles rapidly and is readily soluble in nitric acid. However, this precipitation procedure has the disadvantages of requiring close pH control on "hot" solutions and special acid resistant tanks for the operation.

Another precipitation method, previously investigated by Kellex workers, (see Report KLX-37)[3] involves the addition of excess NaOH to uranium solutions or slurries to precipitate the mixed uranates and phosphates of uranium. However, this precipitate is very finely divided and frequently requires many months to settle. An additional disadvantage is

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Feed Preparation (continued)

that a large quantity of solids will be added to waste volumes that are already near saturation. However, this procedure has an advantage over acid precipitation in that no close pH control is needed, and that the precipitations could be carried out in the present tanks.

The chemical costs for the different feed preparation procedures are summarized in Table 4.0-1 and the procedures are given in Figures 1-7. In preparing a feed containing 120 g/l of uranium from total waste, using NaOH precipitation and HNO_3 dissolution of the precipitate to 3.0 N, the chemical cost was ₡0.27 per kilogram of uranium processed. This cost figure may be decreased slightly if losses higher than 0.05% may be tolerated. The chemical cost of a similar feed using HNO_3 for precipitation was ₡0.31 per kilogram. If H_2SO_4 was substituted for HNO_3 in the precipitation, the feed preparation chemical cost was reduced to ₡0.19 per kilogram. However, excessive quantities of sulfates resulted in the feed unless the precipitates were well washed with mon-sodium phosphate (0.05 M).

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Table 4.0-1

TBP Metal Recovery Process-Chemical Cost Comparison of Alternate Feed Preparation Procedures

Basis: 100 ml laboratory experiments
Feed: Supernatant from Hanford waste tanks 103U and 103T
Total Waste (1) - 0.291 M UO_2^{++} 0.270 M $SO_4^{=}$
3.93 M Na^{+2} 0.729 M $NO_3^{=}$
0.239 M $PO_4^{=}$ 1.29 M $CO_3^{=}$

		Chemical Requirements/Kg. U				U Loss(3) (%)	Final U Conc. g/l	Settling Time Days(2)	Operational Characteristics
		NaOH g	98% H_2SO_4 ml	60% HNO_3 (ml)	Cost/Kg U (Cents)				
Direct Acidification	Total Waste	-	-	7150	48	Nil	50-60	-	Column size and costs would be increased in extraction. Has advantage of simplicity
	103U Sup't.			13800	92		22-30		
NaOH Precipitation	Total Waste	730	-	3220	27		130-140	120	Adds considerable solids to waste streams. Ppt'n could be carried out in present tanks. Ppt settles very slowly.
	103U Sup't	1320		2520	26	0.2	100-110		
HNO_3 Precipitation	Total Waste	-	-	4670	31	0.02	130-140	3	No extra solids added to waste streams.(4) Acid resistant ppt'n tanks req. Ppt settles rapidly.
	103U Sup't.			6170	41	0.1	120-130		
	103T Sup't.			7000	47	0.1	120-130		
H_2SO_4 Precipitation	Total Waste	-	830	2380	19	0.02	130-140	4	Acid resistant ppt'n tanks req. Ppt settles rapidly.
	103U Sup't.		1620	1760	18	0.1	120-130		
	103T Sup't.		2030	1760	19	0.1	120-130		

(1) From Report KLX-37.
(2) These are rough estimates based on qualitative observations on a small scale.
(3) This loss occurs in precipitation with no washing.
(4) Provided HNO_3 may be recovered from the wastes.

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Feed Preparation (continued)

In the feed preparation experiments involving waste supernatant actual samples from Hanford tanks 103 U and 103 T were used. In order that the results involving "total waste" be comparable to the extensive feed preparation experiments carried out by Kellex workers, synthetic total waste solutions were made up as follows (see Kellex Report KLX-37):

Composition of Total Waste

Ionic Constituents	Concentration M/L
UO_2^{++}	0.291
Na^+	3.93
$PO_4^{\equiv}$	0.239
$SO_4^{=}$	0.270
NO_3^-	0.729
$CO_3^{=}$	1.29

After aging (digesting at 70°C) for 10 days this mixture resulted in a slurry containing 69.5 g U/l. After settling, the mother liquor (65% by volume) contained 25.2 g U/l at a pH of 10.6. The specific gravity of the slurry was 1.273 at 25°C.

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5.0 Solvent Studies

The chemical stability of tributyl phosphate - "Varsol" mixtures, under the conditions of the TBP process, has been adequately demonstrated with the solvent being successfully recycled five times. However, future specifications for the tributyl phosphate should exclude butyl alcohol and even traces of the mono and dibutyl phosphates. Cleanup procedures for the used solvent consist of 0.1 volume washes with HNO_3, NaOH, and water. $Cr_2O_7^=$ washes or steam sparging will not be necessary unless the butyl alcohol content builds up appreciably after repeated reuse.

5.1 Solvent Stability and Cleanup Procedures

The stability of tributyl phosphate to nitric acid was satisfactorily demonstrated by refluxing the solvent with an equal volume of concentrated nitric acid for five hours without evidence of appreciable decomposition. However, traces of decomposition products were formed which, upon using the refluxed solvent in subsequent extractions, increased plutonium IV extraction by a factor of fifty. Extraction of beta emitting fission products was also increased by a factor of about 2, whereas uranium extraction was not appreciably affected (see Table 5.1-1).

Since butyl alcohol (and consequently its oxidation products including butyl nitrate) was known to be present the effect of these impurities on the extraction of plutonium IV was observed in controlled batch tests. Also,

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Solvent Stability and Cleanup Procedures (continued)

since mono and dibutyl phosphates (-acid ortho phosphates) could occur in the manufacture and/or in the breakdown of TBP, the effect of these reagents was also tested. Only isobutyraldehyde (see Table 5.1-2) caused a significant drop in plutonium extraction (factor of 50 for Pu IV, factor of 10 for Pu VI). However, even traces of the mono and dibutyl phosphates increased the extraction of plutonium and fission products by factors of 10 to 20. Extraction of uranium was not significantly affected.

In subsequent stripping studies however, it was shown that the back extraction of uranium, plutonium and fission products was not easily reversible from TBP containing mono and dibutyl phosphates. Approximately 90% of the uranium and about 90% of the alpha and beta activity remained with the solvent after four equal volume strips with water and could only be removed by NaOH washes. Uranium holdup in the stripped solvent was also observed for the decomposition products of butyl alcohol but only to the extent of about 0.1% of the amount originally present.

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Table 5.1-1

Effect of Refluxing TBP with HNO_3 on Subsequent Plutonium, Uranium, and Fission Product Distribution Coefficients

Aqueous Phase: Dissolver Solution 100 mg/ml U, 3.0 N HNO_3, Pu^{IV}, 10^6 β c/m/ml

Organic Phase: 15% refluxed TBP-85% Varsol, 0.55 M HNO_3, refluxing time - 5 hrs.

HNO_3 Conc. used in refluxing (M)	Distribution Coefficients in Ext'n*(O/A)				Solvent Reducing Normality Prior to Extraction
	Pu	U	Gross β	HNO_3	
-	0.99	5.35	0.0061	0.031	0.197
-	0.95	5.48	0.0011	0.028	0.244
3	0.74	4.78	0.0084	0.026	0.28
5	0.56	6.96	0.0092	0.026	0.14
7	4.33	4.22	0.0095	0.022	0.18
9	7.04	3.31	0.0089	0.016	0.15
11	10.3	5.13	0.013	0.016	0.21
13	20.77	5.19	0.010	0.011	0.21
16	49.80	8.26	0.011	0.014	0.15

*Values given represent average of duplicate analyses.

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Table 5.1-2

Effect of Butanol Oxidation Products as Impurities on Extraction of Pu with Tributyl Phosphate

Organic Phase: 15% tributyl phosphate
85% Varsol, 0.2 molar in various impurities.
Aqueous Feed: 4.0 M HNO_3, Pu^{IV} tracer
Temperature: 20°C ± 0.2

Impurity added to solvent	Distribution Coefficient(org./aq.) Pu IV	Pu VI
"Control"	10.0	2.9
n-butyric acid	7.52	1.7
iso-butyric acid	7.58	1.7
n-butyraldehyde	7.76	1.5
iso-butyraldehyde	0.19	0.23
n-butyl alcohol	7.80	1.7
iso-butyl alcohol	8.14	1.8
butyl nitrate	9.9	2.3

[redacted]

Solvent Stability and Cleanup Procedures (continued)

Investigations of simple cleanup procedures for used solvent mixtures (see Table 5.1-3) indicate that a 1.0 M nitric acid wash, followed by two 1.0 M NaOH washes, and two H_2O washes are sufficient to restore the solvent to its initial quality. When a solvent mixture of high initial quality is finally obtained it is believed that even less vigorous washing may make the solvent ready for reuse.

The question as to how long a solvent mixture may be used before cleanup is necessary is still undecided. Operations in the Semi-Works columns have shown that probably as many as 10 recycles of the solvent are feasible before an appreciably build-up of deleterious impurities occurs.

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Table 5.1-3

Effect of Solvent Pretreatment Procedures on Uranium, Plutonium, and Fission Product Extraction by TBP

Aqueous Phase: Uranium dissolver solution, 3.0 M HNO_3, spiked with mixture of Pu^{IV} and Pu^{VI}

Organic Phase: One equal-vol. of 15% TBP Varsol Mixtures

TBP Pretreatment	Distribution Coefficients (org./aq.) Pu*	UO_2^{++}	Gross Beta
Steam sparging	2.7	10.9	0.008
0.1 M $Cr_2O_7^{=}$, 0.1 M HNO_3 washes followed by 0.1 M NaOH and H_2O washes	2.4	11.4	0.008
1 M NaOH and H_2O washes	3.9	12.1	0.008
0.1 M $NaHSO_3$ and H_2O washes	3.0	12.2	0.008
0.1 M Na_2CO_3 and H_2O washes	3.1	12.3	0.007
No treatment commercial grade TBP used	3.8	15.6	0.01

5.2 Solvent Specifications

Based on laboratory batch extraction and stripping data, the following have been established as tentative specifications for tributyl phosphate to be used in the waste metal recovery program:

1. Reducing normality less than 0.001 (i.e. free of butyl or isobutyl alcohols).
2. Zero acidity i.e. free of the mono and dibutyl acid ortho-phosphates (mono and dibutyl phosphates).

Conformance to these specifications yields increased decontamination in extraction and reduced losses in stripping.

Specifications for the diluent have not been finally established but empirical laboratory experiments have shown that a low Kauri butanol number[9] is important (i.e. of the order of 30). Although this is a rather crude criterion of the aromaticity or solvent action of the compound, it is nevertheless used rather widely in that sense by the producers of the diluents that are of interest.

The Kauri butanol value is specified as the amount of a given solvent that can be added to a standard Kauri gum solution in butanol to produce a definite turbidity, as compared with the amount of C.P. benzene used in a similar titration and arbitrarily taken as 100 percent standard.

Most aromatic compounds are probably undesirable as a diluent constituent because of their greater reactivity with strong HNO_3. Experiments with "Varsol" have shown that once the aromatic components were

Solvent Specifications (continued)

removed by sulfonation, the remaining fractions were very stable even with concentrated HNO_3.

Another variable may be eventually incorporated as a diluent specification which involves the "average" or apparent dipole moment. Reference to Table 5.2-1 shows that highly non-polar, symmetrical compounds yield the greatest uranium extraction under a given set of conditions. Polar compounds, like chloroform, should definitely not be used since they apparently complex TBP and decrease its effective concentration. However, the equilibration time of this experiment (10 minutes) was not sufficiently long to eliminate the effects of slow diffusion rates.

Table 5.2-1

Effect of Diluent Composition

On Uranium Extraction

With TBP

Organic Phase: 10% TBP in various diluents
Aqueous Phase: 0.1 M U, 3.0 M HNO_3
Temperature: 20°C ± 0.5°
Equilibration Time: Ten minutes.

Diluent	Uranium Dist. Coeff. (org./aq.)
"Gulf BT"	3.81
"Varsol 111"	4.48
"Varsol 107"	3.86
Hexane	3.71
Heptane	3.71
Octane	2.50
Decane	3.80
Benzene	4.47
Methyl cyclo hexane	4.2
Carbon tetrachloride	4.22
Chloroform	0.55
Trichloro ethylene	1.69

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Solvent Specifications (continued)

Physical specifications for the diluent include (1) low specific gravity (less than 0.8) (2) stability to strong nitric acid and (3) a fairly high flash point i.e. greater than 35°C.

The initial experimental work with TBP was carried out using hexane as a diluent. Although very stable to HNO_3, its low flash point (15.5°C) and boiling point (69°C) made this an undesirable solvent for a plant scale process.

Subsequent process studies have been carried out using "Varsol" and "Gulf BT" (Sp. G. 0.75) both of which are petroleum cuts very close to kerosene. "Varsol" has a flash point of 49°C and boils in the range of 167-180°C. "Gulf BT" has similar physical and chemical properties.

"Varsol" is reported by the vendors as consisting of approximately 60% paraffins, 30% naphthenes and the remaining 10% as aromatics. However each of these components may vary by several percent. One component, probably the aromatics and/or branched chain paraffins, has been observed to react with nitric acid at concentrations greater than 9.0 N even at room temperatures. However, once this component is removed by continued reaction with strong acid, the remaining components are very stable and do not absorb fission products even after prolonged contact with TBP process solutions (greater than 100 hours).

A program is underway to establish the deleterious component of the solvent and have it removed by the vendor if feasible. Efforts will continue, however, to find an even more satisfactory diluent.

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5.3 Analytical Procedures

Very wide variations have been observed in the specific gravity of various solvent diluents (Varsol, Gulf BT, etc.) used in the TBP metal recovery process (0.76 - 0.79). Some variation in specific gravity has also been observed in different TBP samples. This fact make specific gravity an unreliable indication of the true concentrations of TBP and diluent in "fresh" solvent mixtures. This procedure is equally unreliable in the analyses of "used" solvents mixtures since varying amount of H_2O, HNO_3 and U are present.

The following method was devised to provide a rapid approximate analytical procedure of sufficient accuracy to be used in process studies:

Prepare a saturated solution of uranyl nitrate which is 1-3 normal in nitric acid. (It is advantageous to have solid particles of $UO_2(NO_3)_2 \cdot 6 H_2O$ present). Agitate this uranium slurry with an equal volume of the organic phase for 1-3 minutes. Separate the two phases, centrifuge the organic layer, and analyze for uranium concentration.

$$\% \text{ TBP} = \frac{\text{mg U/ml of org. phase}}{4.38}$$

This expression is based on the fact that the saturation solubility of uranium in TBP is two mols of TBP/mol of U or 532 g TBP/238 g U. To convert this term to percent by volume, 0.976 was used as the density of TBP at 25°C. Thereby a 100% TBP solution is 3.67 M and 1 ml of 1% TBP should dissolve 0.0184 millimoles of uranium or 4.38 mg.

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Analytical Procedures (continued)

The indirect method proposed here has one disadvantage in that appreciable quantities of uranium-extracting impurities would cause an error. Another small error also arises in that a volume change (1-5%) occurs in the organic phase (about 5% for 15% TBP) on becoming saturated with uranium. Consequently, a correction factor would be necessary for very accurate work. However, the above expression has been found accurate to within ± 0.5% TBP in the TBP range of 1 - 30%.

A colorimetric procedure for total $PO_4^{\equiv}$ following a Parr bomb fusion is being investigated by the analytical section of the Chemistry Division but results to date are not very satisfactory. A more accurate procedure based on readings of the dielectric constant has been developed by M. T. Kelley and P. F. Thomason of the Chemistry Division[6]. The method is fairly rapid but requires a prewashing procedure for used solvent mixtures and rather careful calibration curves.

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6.0 Plutonium and Fission Product Studies

The extraction of Pu^{IV} and Pu^{VI} by TBP is a reversible reaction that is practically as rapid as that of UO_2^{++}. The presence of even traces of impurities prevents an exact determination of the distribution coefficients. Evidence has been obtained that Pu^{VI} is reduced on prolonged contact with the solvent mixtures. Also, the extraction of both Pu^{IV} and Pu^{VI} is greatly increased by the presence of mono and dibutyl phosphates (see Section 7.3). Apparently, at acidities of approximately 0.5 molar the extraction of both the four and six states are nearly equal (see Table 6.0-1). At very high HNO_3 concentrations (above 4.0 M) the distribution coefficients for Pu^{IV} are greater than Pu^{VI} by factors of 5 to 10. The distribution coefficients (org./aq.) for Pu^{III} are quite low (of the order of 0.01) in 1.0 N nitric acid.

For Pu^{IV} in acid solutions greater than 1.0 N an equation involving a second power TBP dependence and fourth power nitrate dependence satisfies most of the data with a value of K_m of about 3.0. However, the results at lower acidities are not in agreement, which again may be due to the presence of unremoved impurities in the solvents, or to hydrolysis of Pu.

In the presence of uranium, plutonium extraction is greatly depressed. (see Table 6.0-3) Consequently, any attempt to extract plutonium simultaneously with uranium could only be accomplished by careful adjustment of conditions[5].

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Plutonium and Fission Product Studies (continued)

Analyses of ruthenium in tributyl phosphate are somewhat difficult, but results based on gross counting of tracer ruthenium indicate this element has distribution coefficients (org./aq.) of less than 10^{-4} in the acid range of 1-5 normal. In the same range of acidity zirconium distribution coefficients varied from 0.08 to 0.7 (see Table 6.0-4). However, there was appreciable variation of these values depending on the grade of tributyl phosphate used. Adequate solvent cleanup procedure may improve overall decontamination from zirconium. In the presence of uranium the extraction of zirconium was depressed by factors greater than 10 when the organic phase was 80% saturated in uranium (see Table 6.0-5).

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Table 6.0-1

Effect of HNO_3 on Pu^{IV} Extraction With

15.4% Tributyl Phosphate - 84.6% Gulf BT*

Initial HNO_3 Conc. (M)	Dist. Coeff. (org/aq)			HNO_3 Distribution	
	Pu^{III}	Pu^{IV}	Pu^{VI}	Org. Phase	Aq. Phase
0.11	0.003	0.005	0.01	~ 0.002	0.098
0.30	-	0.06	0.005	0.010	0.300
0.50	0.01	0.13	-	0.026	0.475
0.82	-	0.40	-	0.055	0.770
1.1	0.03	0.83	0.51	0.090	1.02
1.60	-	1.54	-	0.140	1.46
2.03	-	1.75	1.01	0.188	1.84
2.3	-	2.85	-	0.220	2.11
3.1	-	3.54	1.4	0.290	2.81
3.9	-	6.02	-	0.365	3.54

* Solvent was prewashed with 1.0 NaOH, followed 4 washes with H_2O.

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Table 6.0-2

Effect of TBP Conc. on Plutonium Extraction

Aqueous Phase: 1.85 M HNO_3, Pu tracer

Organic Phase: TBP-Gulf-BT Mixtures

Temperature: 20°C

TBP Conc. (Volume %)	Pu Distribution Coefficient (Org./Aq.)	
	Pu^{IV}	Pu^{VI}
2.05	0.04	0.04
5.13	0.31	0.21
10.27	1.45	0.58
15.40	1.90	0.95

Table 6.0-3

Effect of Uranium Concentration on

Plutonium Extraction

Aqueous Phase: Pu tracer, 3.0 M HNO_3, U

Organic Phase: 15% TBP-85% Varsol

Temperature: 20°C.

Aqueous Uranium Concentration mg/ml	Distribution Coefficients (Org./Aq.)	
	Pu^{IV}	Pu^{VI}
20	2.26	0.91
40	1.13	0.56
80	0.34	0.16
100	0.23	0.11
200	0.11	0.04

Table 6.0-4

Effect of HNO_3 on Ru and Zr Extraction

by

Tributyl Phosphate

Feed: ~~0-5N HNO_3~~, tracer Ru and Zr

Solvent: 15% Bu_3PO_4-85% Varsol.

~~Equal volume equilibrations at 20°C for five minutes.~~

HNO_3 N	Zr Dist. Coeff. ~~(gross β)~~ (Org.Aq.)	Ruthenium Dist. Coeff. ~~(Org./aq.)~~ ~~(1)~~	(2)*
0.0	0.08	0.00053	-
0.1	0.08	0.00041	-
0.5	0.06	0.00073	-
1.0	0.07	0.00077	-
2.0	0.11	0.00083	-
3.0	0.16	0.00055	0.75
5.0	0.72	0.00084	0.31

~~1. Ruthenium tracer in nitric acid, probably tetravalent.~~

2. These feeds contained 0.02M periodic acid, ruthenium was probably in the octavalent state.

Table 6.0-5

Effect of Uranium on Zr and Ru Extraction by Tributyl Phosphate

Feed: 5.2N HNO_3, 20-200 mg/ml U, tracer Ru and Zr.
Solvent: 15% Bu_3PO_4-85% Varsol
Equal volume equilibrations at 20°C for five minutes.

Solvent Saturation in Uranium (%)	Zr Dist. Coeff. (Gross β) (org./aq.)	Solvent Sat. in Uranium (%)	Ru Dist. Coeff. (Gross β) (Org./aq.)
0	0.7	-	-
31	0.30	36	0.00122
53	0.088	63	0.00158
69	0.030	80	0.00081
78	0.028	85	0.00064
80	0.031	91	0.00069
80	0.024	90	0.00049

[redacted]

7.0 Laboratory Countercurrent Runs

Laboratory countercurrent studies on the TBP Process have been continued in cooperation with pilot plant column runs. The results have demonstrated:

1. That an almost unlimited number of "flowsheets" are operable using almost any feed makeup in the uranium concentration range of 20-140 g/l. Decontamination factors of 2×10^4 are consistently obtained with overall U losses of about 0.2% through one cycle.
2. (a) That a column "H.E.T.S." is equivalent to about 3.5' using acidified Hanford waste supernatant solutions as a feed stream and 1/4" x 3/8" split rings for packing. (H.E.T.S. values using ORNL waste solutions were previously reported as ca 2.5').

   (b) That an absolute minimum of five extraction stages is necessary to obtain a uranium loss of 0.1%.
3. That adequate plutonium decontamination (1 part in 10^8) can be obtained using 0.05 M ferrous sulfamate in the scrub section (using at least 4 scrub stages).
4. That it may be feasible to recover as much as 90% or greater of the plutonium present in Hanford wastes with the addition of one more column.

[redacted]

[redacted]

Laboratory Countercurrent Runs (continued)

5. No time dependence on stripping was observed in the interval of 10 seconds to 3 minutes.
6. In feed solutions containing 2.0 M sulfates, using only 3.0 M nitric acid as a salting agent, uranium losses were less than 0.1%.
7. In feed solutions containing 0.4 M $PO_4^{\equiv}$ and no salting agents other than 3.0 M HNO_3, uranium losses were less than 0.1%. At higher $PO_4^{\equiv}$ concentrations it was necessary to increase the nitric acid to as much as 5 N to obtain corresponding losses. However, in the presence of $NaNO_3$ the nitric acid requirements were considerably reduced.

7.1 Observations on H.E.T.S. Values

Laboratory countercurrent batch studies carried on simultaneously with the pilot plant column runs (see Report C. F. 49-11-177)(7) proved very valuable and indicate a large variety of possible "flowsheets" (see Figures VIII, IX, X, pp. 54, 55, 56).

Using solutions from the TBP column feed streams it was demonstrated that the column extraction losses occurring in the first five runs corresponded to only three plus batch stages (see Table 7.1-1). These data indicated that:

[redacted]

[redacted]

Table 7.1-1

Determination of Column H.E.T.S. by Comparison with Counter-Current Batch Extraction Stages

Run No.	Aq. U Concentration Per Batch Stage (mg/ml)				U Conc. in Col. A.W. (mg/ml)	Apparent Number of Col. Stages(1)	Col. Ex'tn Height (ft)
	1	3	5	6			
1	14.50	0.558	0.018	0.008	0.5	3+	12.5
2	12.25	0.480	0.027	0.002	0.481	3	12.5
3	7.13	0.375	0.187	0.079	0.07	ca. 5.0	12.5
4	13.00	0.147	0.016	0.014	0.074	3+	12.5
5	15.25	0.218	0.056	0.020	0.21	ca. 3.0	12.5
6	16.78	0.220	0.032	0.012	0.038	5	17.5
7	5.55	0.163	0.044	0.016	0.026	5+	17.5
8	3.50	0.070	0.024	0.018	0.024	5	17.5
9	-	-	0.03	-	0.032	5	17.5

[redacted]

[redacted]

Observations on H.E.T.S. Values (continued)

(a) since there were 12 feet of packed extraction section (1/4" x 3/8" split rings) an "average" theoretical stage must be equal to about 3.8-4.0 ft. or (b) channeling was occurring in the packing.

Upon extending the extraction column by 5.5 ft. (to 17.5') two additional stages were produced in the column indicating that probably both effects were responsible and that 3.5 feet more nearly represents an "average" HETS in this system. In the 1 1/2" column studies with ORNL wastes (see pp. 59-61), using 1/4" x 1/4" packing, somewhat shorter H.E.T.S. values were observed (i.e. 2.5' at 25% of flooding and 3.0' at 50% of flooding).

7.2 Flowrates

The average variation of uranium distribution coefficients with stage number is shown in Figure XI, page 57. This figure illustrates the criticality of flowrates if less than five extraction stages were being used.

In establishing the TBP concentration to be used for a particular run the flowrate to be used must be balanced against the concentration. That is, it is desirable to operate at as high a concentration of TBP as possible to reduce the total flow necessary. On the other hand, the concentration cannot exceed 15% appreciably without encountering stripping or

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Flowrates (continued)

emulsion difficulties. Suppose on a given run that 60 g/l of uranium is entering the feed plate, at 60 cc/min. To keep from "pushing" uranium out the bottom of the column a solvent mixture is needed that is capable of removing 60 x 60 or 3600 mg/min. (disregarding the amount (usually about 10%) that the scrub will reflux). One milliliter of a one percent TBP solution can carry (70% saturated) 4.2 x 0.7 = 2.94 mg/ml or 1225% ml/min. Using a 10% TBP solution, a flow of 122.5 ml/min. would be required. Using a 13% TBP solution, 94 ml would be adequate, and so on.

Variations in this flow of 10% are not serious, provided adequate stages are provided i.e. at least 5 or 6.

[redacted]

[redacted]

7.3 Plutonium Decontamination and Recovery

Adequate plutonium decontamination (1 part in 10^8 of uranium) was demonstrated by adding ferrous sulfamate to the scrub solution, provided as many as four scrub stages were used. However, controlled studies (see Table 7.3-1, Fig. XII) have indicated that ferrous sulfamate deteriorates rather rapidly, even at room temperature, in strongly acid solutions (3 normal and higher), and will have to be renewed after about 40 hours, or continuously fed to the streams. Although this is not too disadvantageous the investigation of more stable holding reductants will be undertaken. In any case, the possibility of eliminating the scrub section entirely will be studied since adequate plutonium decontamination may be achieved in extraction. This change would not appreciably alter the overall decontamination of uranium from fission products in old wastes since factors of only 2 or 3 are obtained in the scrub section.

Laboratory countercurrent runs have also shown that from 80-90% of the plutonium is extracted from feed solutions as high as three normal in acid. This raises the possibility of recovering an appreciable fraction of the Pu with no significant changes in the present process. With the elimination of the scrub section, the AP stream containing uranium and plutonium could be passed directly into a packed column to be contacted with ferrous sulfamate. The plutonium would be reduced and

[redacted]

[redacted]

Plutonium Decontamination and Recovery (continued)

stripped, the uranium remaining with the organic stream to be stripped in a third column. Scouting studies have been carried out which indicate that this is feasible and that this amount of plutonium recovery may be expected with no further changes in the process conditions.

[redacted]

[redacted]

Table 7.3-1

Stability of Ferrous Sulfamate in Strong Nitric Acid Solutions

Feed:	Organic
U-0.246M	13% TBP
Pu^{IV}-$6x10^5$ Pu c/m/ml	87% Varsol
$Fe(NH_2SO_3)_2$-0.05 M	

Time Elapsed After Adding $Fe(NH_2)_2SO_3$ Hrs.	Nitric Acid Concentration in Feed					
	1N-HNO_3		3N-HNO_3		5N-HNO_3	
	Feed R-N*	Pu Ext'd c/m/ml	Feed R-N*	Pu Ext'd c/m/ml	Feed R-N*	Pu Ext'd c/m/ml
20	0.049	520	0.049	460	0.044	590
23	0.049	540	0.049	540	0.049	690
42	0.050	530	0.046	550	0.029	810
43	0.050	530	0.046	740	0.029	2300
66	0.049	550	0.049	820	0.024	2600

* R-N refers to reducing normality.

[redacted]

[redacted]

7.4 Effect of Phosphate and Sulfates on Uranium Recovery

Adequate uranium recovery (99.9%) was obtained at the concentrations of $PO_4^{\equiv}$ and $SO_4^{=}$ encountered in HW waste solutions (i.e. less than 0.4 M for each anion). Higher concentrations (0.4-.7M) are permissible with increased feed acidities. For ORNL waste and H.W. supernatant waste, 2.5-3.0M acid was adequate because of the high $NaNO_3$ concentration present. In the case of Hanford sludge, additional nitric acid may be necessary to break up the uranium complex formed by these ions. Nitric acid would tend to dissociate this complex as follows:

$$(UO_2)_3(PO_4)_2 + 6HNO_3 \rightleftharpoons 3(UO_2)(NO_3)_2 + 2H_3PO_4$$

$$(UO_2)(H_2PO_4)_2 + 2HNO_3 \rightleftharpoons (UO_2)(NO_3)_2 + 2H_3PO_4$$

$$(UO_2HPO_4) + 2HNO_3 \rightleftharpoons (UO_2)(NO_3)_2 + H_3PO_4$$

the phosphoric acid being largely undissociated at very high concentrations of HNO_3. This effect was shown in a series of countercurrent batch runs with varying concentrations of $PO_4^{\equiv}$ and $SO_4^{=}$ in the feeds.

If the phosphate content were of the order of 0.4 M, 3 molar nitric acid was required to obtain a uranium loss of approximately 0.1% in six extraction stages. However, for $PO_4^{\equiv}$ concentrations of 0.6-0.7 M, nitric acid concentrations of 5-6 molar were necessary to reduce uranium losses to the order of 0.1% (see Table 7.4-1). This required quantity of acid was correspondingly reduced if nitrate were present from other salts. Sulfates in concentrations up to 1.34 M were not deleterious provided the acidity in extraction was at least 3.0 M (see Table 7.4-2).

[redacted]

[redacted]

Table 7.4-1

The Effect of Phosphate Concentration in Aqueous Feed on the Extractability of Uranium in the Waste Metal Recovery Process

Feed (2 volumes): 0.525 M U
Scrub (1 volume): 3 M HNO_3
Solvent (6 volumes): 15% TBP-85% Varsol
Countercurrent batch extraction

Run No.	Conc. $PO_4^{\equiv}$		Conc. HNO_3 M		% U	Stages	
		Extraction		Extraction			
	Feed	Section	Feed	Section	Losses	Ext.	Scrub
1	1.0 M	0.67 M	6.13	5.09	2.00	6	4
2	1.0 M	0.67 M	5.13	4.45	4.30	8	0
3*	1.0 M	0.67 M	5.00	4.43	0.13	7	4
4	0.8 M	0.53 M	5.95	4.97	0.23	6	4
5	0.6 M	0.40 M	5.00	4.33	0.057	6	4
6	0.5 M	0.33 M	5.25	4.50	0.40	6	4
7	0.5 M	0.33 M	3.00	3.00	0.22	6	4

* 1.0 M $NaNO_3$ used as salting agent in addition to HNO_3.

[redacted]

[redacted]

Table 7.4-2

The Effect of $SO_4^{=}$ Concentration On The Extractability of Uranium In The Waste Metal Recovery Process - Six Extraction And Four Scrub Stages In Each Batch Countercurrent Run

Run No.	Conc. $SO_4^{=}$ M		Conc. HNO_3 (M)			Conc. U-M	Conc. of $(C_4H_9O)_3PO_4$ (%)	Flowratio		% U Loss
	Metal Feed	Ext'n Section*	Feed	Ext'n Section*	Scrub			Feed	Org.	
1	1.0 M	0.67	4.50	4.05	3.15	0.525	15	1	2	0.006
2	1.0	0.67	2.95	3.0	3.15	0.525	15	1	2	0.012
3	2.0	1.34	5.10	4.45	3.15	0.525	15	1	2	0.005
4	2.0	1.34	2.90	2.93	3.00	0.525	15	1	2	0.030
5	2.0	1.34	2.80	2.86	3.00	0.10	12.5	1	1	0.200

* Calculated values.

[redacted]

[redacted]

7.5 Flowsheets

Countercurrent batch runs were successfully carried out using feeds verying from 20-92 grams of uranium per liter, on both ORNL and Hanford Works Waste (see Figures VIII, IX,X). Concentrations of 140 g/l were demonstrated as feasible on synthetic HW and ORNL wastes and will be investigated with Hanford sludge as soon as it is available.

A final flowsheet depends almost entirely upon the method used in removing the waste from the tanks (i.e. feed preparation). Consequently the major effort has been devoted to demonstrating the operability of the process through the range of possible conditions rather than for a specific set of conditions that may never be encountered in practice.

A "flowsheet" is most easily characterized by the concentration of uranium in the feed. A feed containing 20 g/l of uranium corresponds to the concentration to be encountered by the direct acidification of very dilute total waste, or supernatant and represents the most pessimistic set of conditions that could be encountered. A flowsheet involving a feed of 60 g/l of uranium represents the optimum condition that would result from direct acidification of "total waste". A feed containing 90-130 g/l of uranium would result from concentrating the uranium by some precipitation procedure, or by directly acidifying sludge alone.

In practice, the final process may involve either, or a combination of all of these different "flowsheets".

[redacted]

Table 7.5-1

TBP Process Countercurrent Batch Extraction Runs on H.W. Waste

Organic flowrate calculated to give ca. 70% saturation at the feed plate.

Organic: Feed: Scrub: Strip Ratio 3:2:1:3 in all runs

6 extraction stages, 4 scrub stages, 4 strip stages

Run No.	Feed			Scrub	Solvent	Decontamination Factor		U-Losses	
	Source	M HNO_3	U g/l	HNO_3 (M)	% TBP by vol.	β c/m/mg U in Product	Overall	Extraction	Strip
1	H.W. Spnt	4.00	21.95	0.99	10%	13.10	1.42×10^4	0.05*	Too low to read
2	" "	4.10	21.50	1.00	10%	7.31	2.83×10^4	0.015*	0.10
3	" "	4.00	20.84	2.00	10%	9.50	3.4×10^4	0.55**	0.49
4	H.W. Spn't. + UNH	3.00	57.50	3.00	13%	4.20	3.0×10^4	0.04	0.14
5	H.W. Spn't. + UNH	3.00	57.50	1.80	13%	5.90	2.3×10^4	0.05	0.15
6	H.W. Spn't. + UNH	2.90	58.50	2.70	13%	3.93	3.55×10^4	0.03	0.126
7	H.W. Spn't.	3.95	21.90	2.00	10%	9.49	2.55×10^4	0.11	0.25
8	H.W. Spnt	3.95	26.00	2.00	10%	6.51	3.08×10^4	0.03	0.24

* There was evidence that these runs were not in equilibrium and that much longer periods of operation would have resulted in high losses.

** An analytical error is believed to be responsible for this result.

[redacted]

7.6 Volume Reduction of TBP Wastes by Evaporation

Using the TBP wastes from countercurrent batch runs, the amount of volume reduction by alkaline evaporation of the process wastes was determined for four flowsheets involving four methods of feed preparation. The volume reduction factors are expressed as % of the original total waste volumes (after neutralization and subsequent evaporation of the process wastes). The results are summarized as follows:

1. Direct acidification of total waste to 3.0 N HNO_3 - 125-135%.
2. Direct acidification of total waste to 2.0 N HNO_3, and concentration by evaporation - 110-120%.
3. NaOH precipitation of total waste and dissolution of the precipitate to 3.0 N HNO_3 - 85-95%.
4. HNO_3 precipitation of total waste and dissolution of the precipitate to 3.0 N HNO_3 - 85 - 95%.

7.7. Specific Gravities and Viscosities of TBP Process Streams

In order that Semi-Works personnel might have approximate Sp. G and viscosity data for the selection of the correct range of instruments for metering process streams, viscosity and Sp. G. data were obtained at 25°C, the data are summarized in Table I.

[redacted]

Table 7.7-1

Relative Viscosities and Specific Gravities of TBP Process Streams at 25°C

With Varying Methods of Feed Preparation

Basis: Synthetic HW Total Waste

Property Measured	Feed Preparation Method								
	Direct Acidification (55 g/l of U)		NaOH Precipitation (140 g/l of U)			HNO_3 Precipitation (140 g/l of U)		
	AF	AW	AF	AW	BW	AF	AW	BW
Sp. G.	1.304	1.193	1.442	1.223	0.843	1.430	1.20	0.850
Rel. Visc.	1.95	1.506	2.71	1.58	1.34	2.59	1.56	1.39

[redacted]

Figure 1

TBP PROCESS FEED PREPARATION BY NaOH PRECIPITATION

Basis: 100 ml of synthetic Hanford total waste
70 g/l U
(65 ml of supernatant)
(35 ml of sludge)

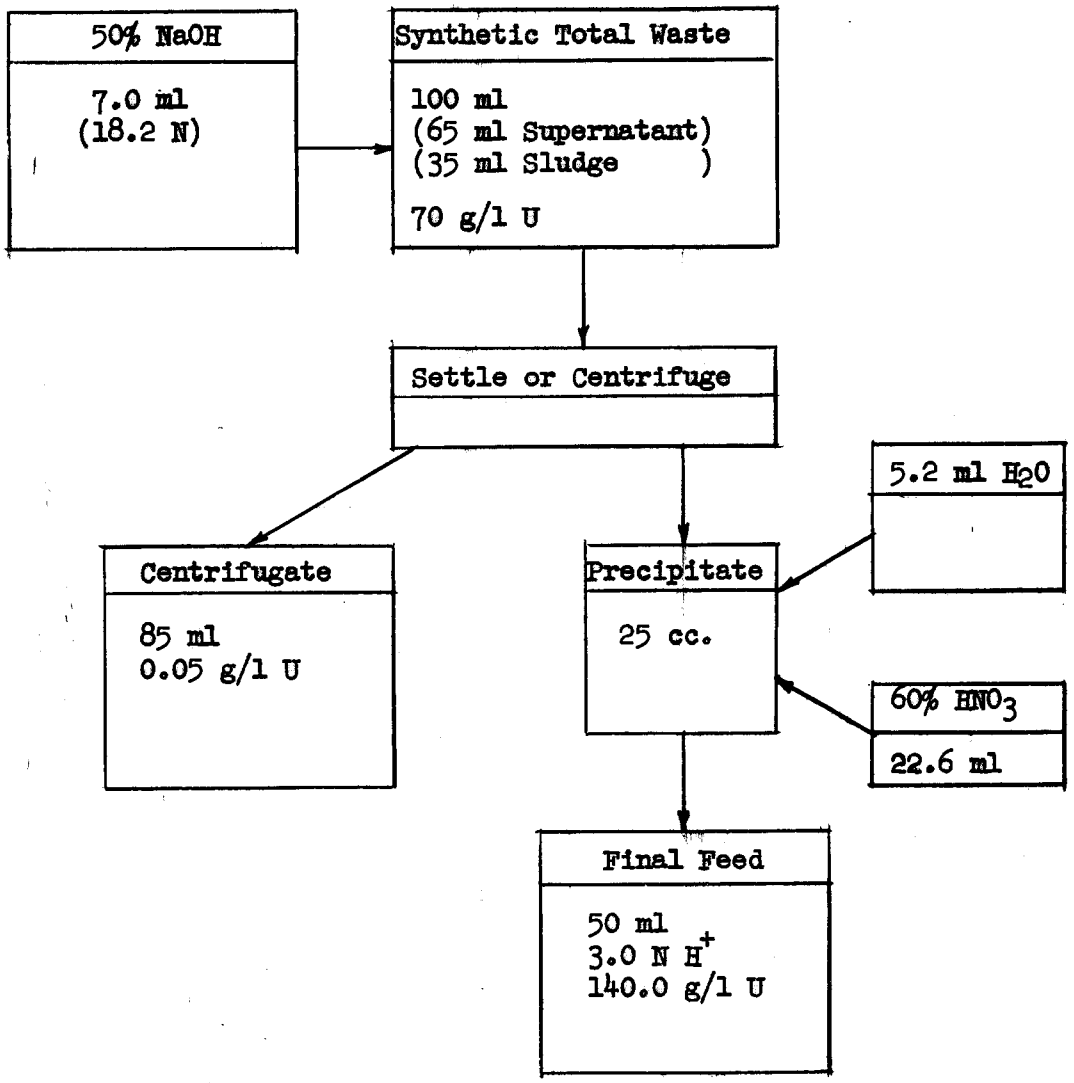

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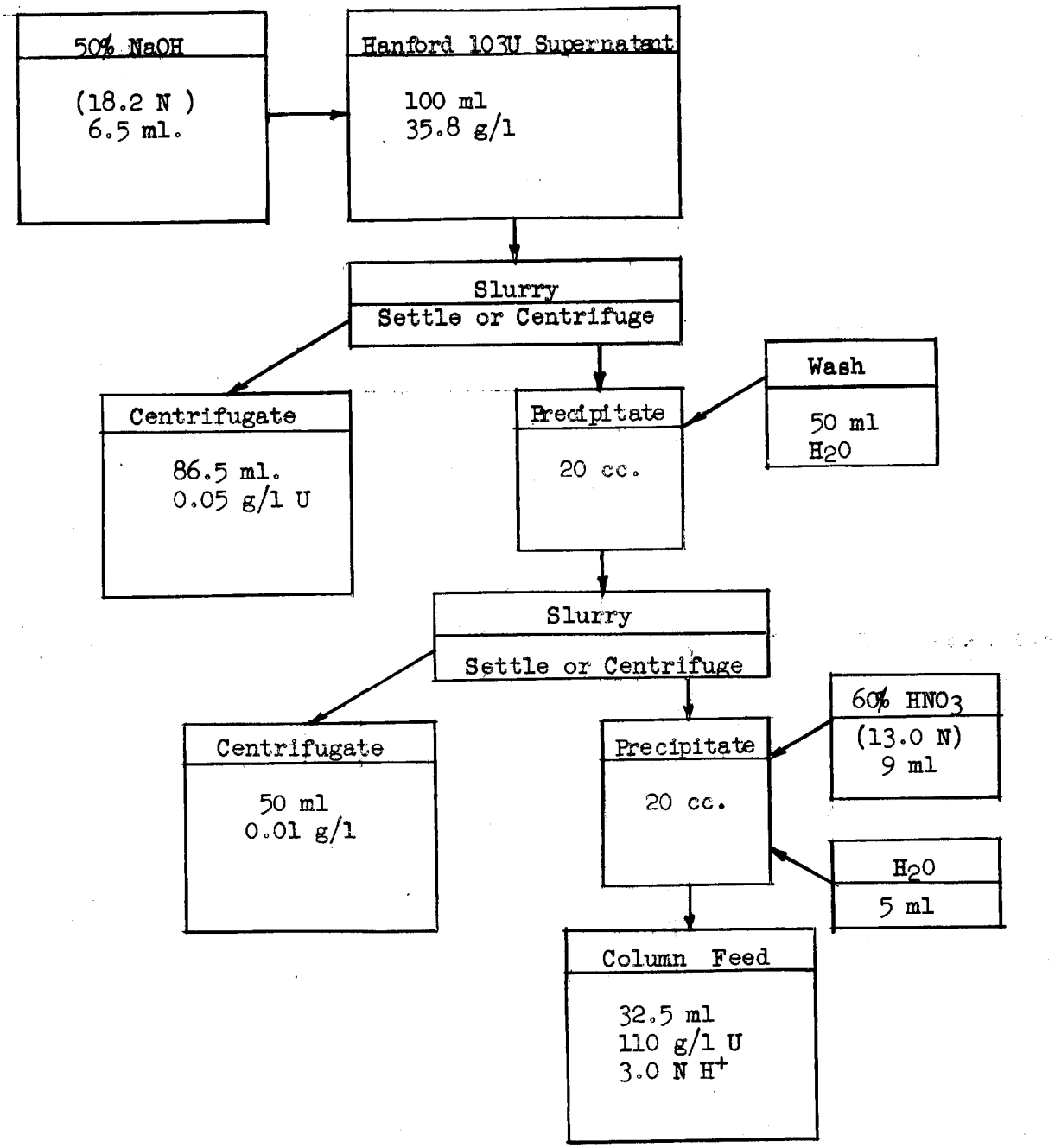
Figure 2

TBP PROCESS FEED PREPARATION BY NaOH PRECIPITATION

Basis: 100 ml of Harford 103 U Supernatant

35.8 g/l U



[redacted]

Figure 3
TBP PROCESS FEED PREPARATION

By

H_2SO_4 Precipitation

Basis: 100 ml of Synthetic Hanford Total Waste

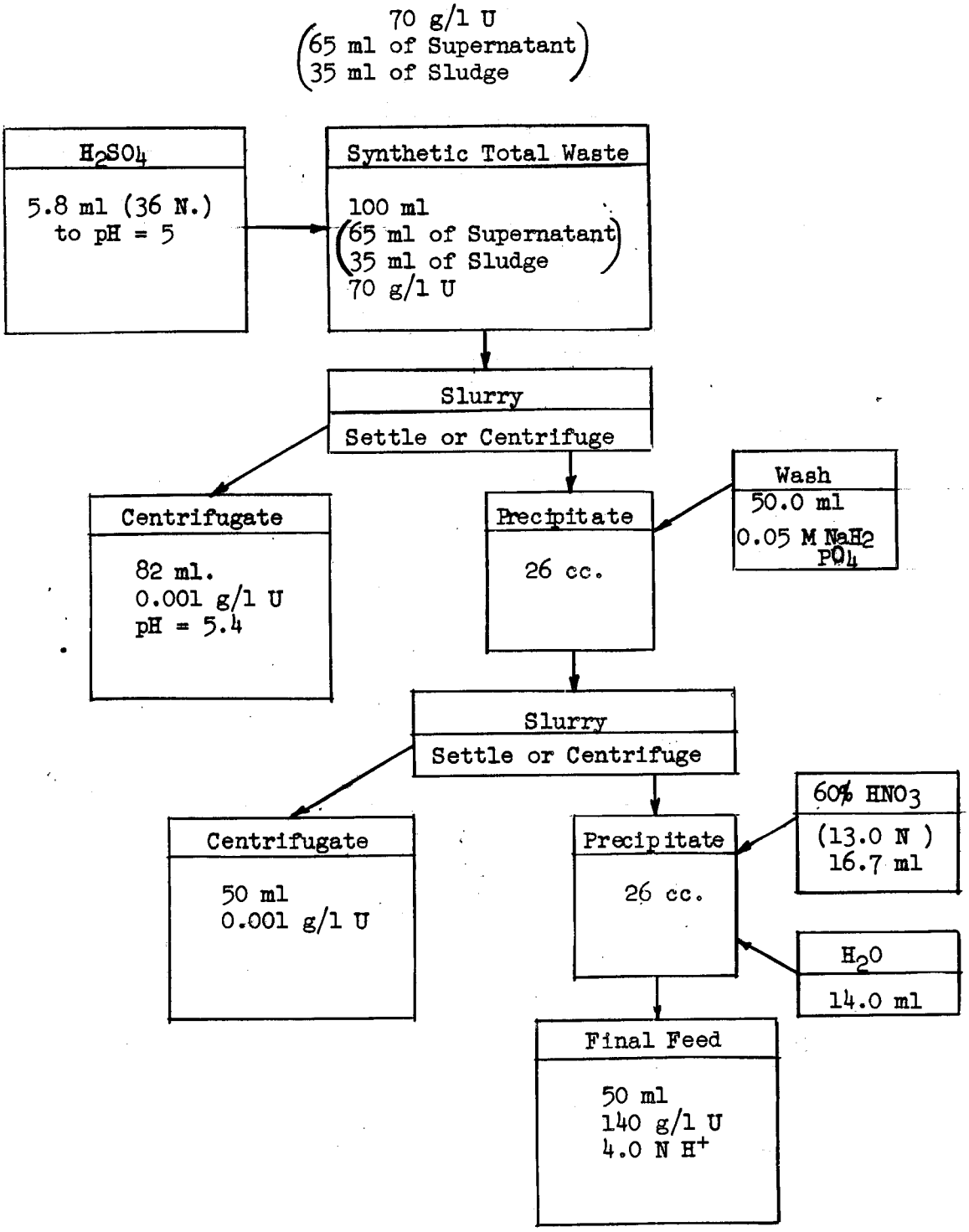


Figure 4

TBP PROCESS FEED PREPARATION

by

H_2SO_4 Precipitation

Basis: 100 ml of Hanford Supernatant (103 U or 103 T)

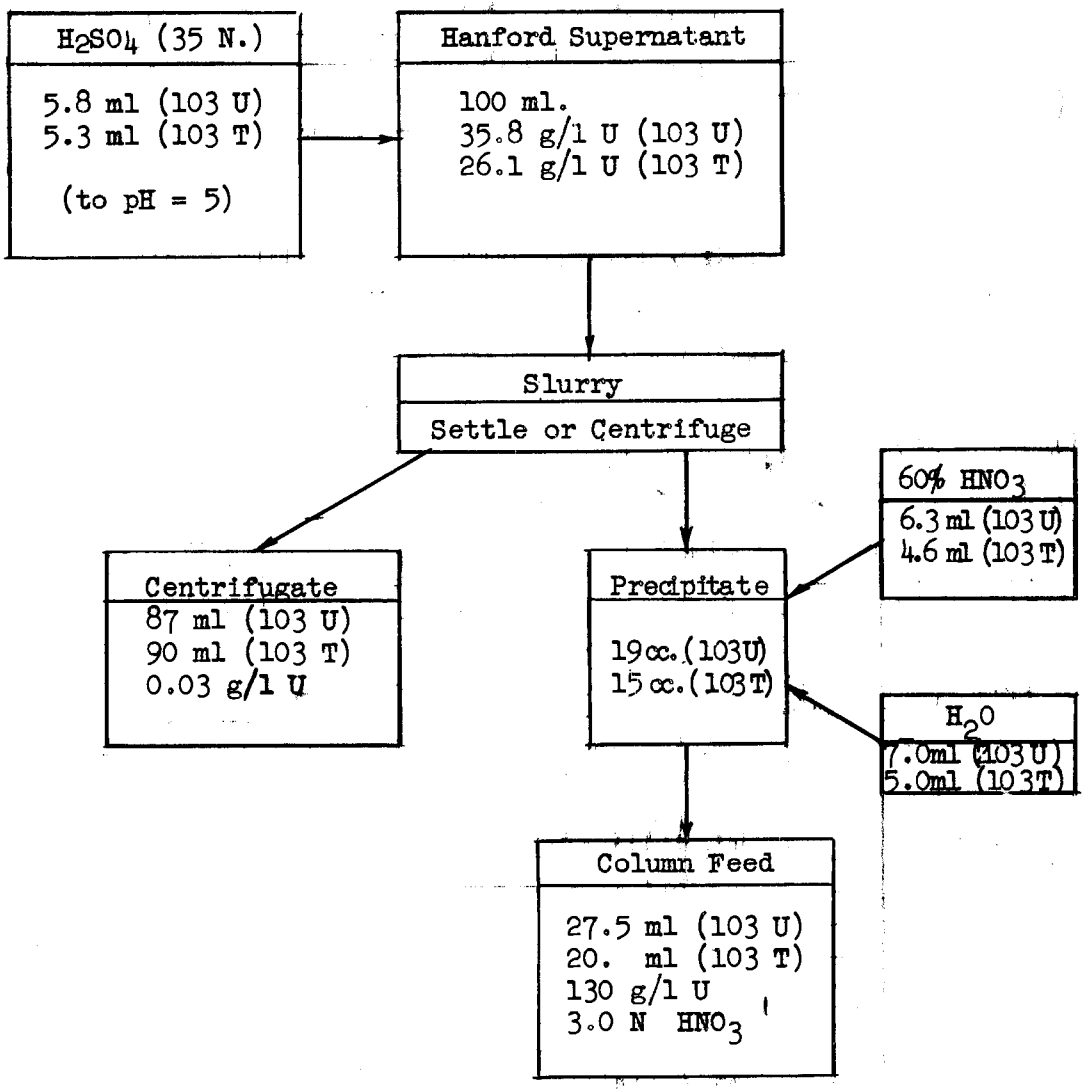


Figure 5

DIRECT ACIDIFICATION AND EVAPORATION OF HW TOTAL WASTE

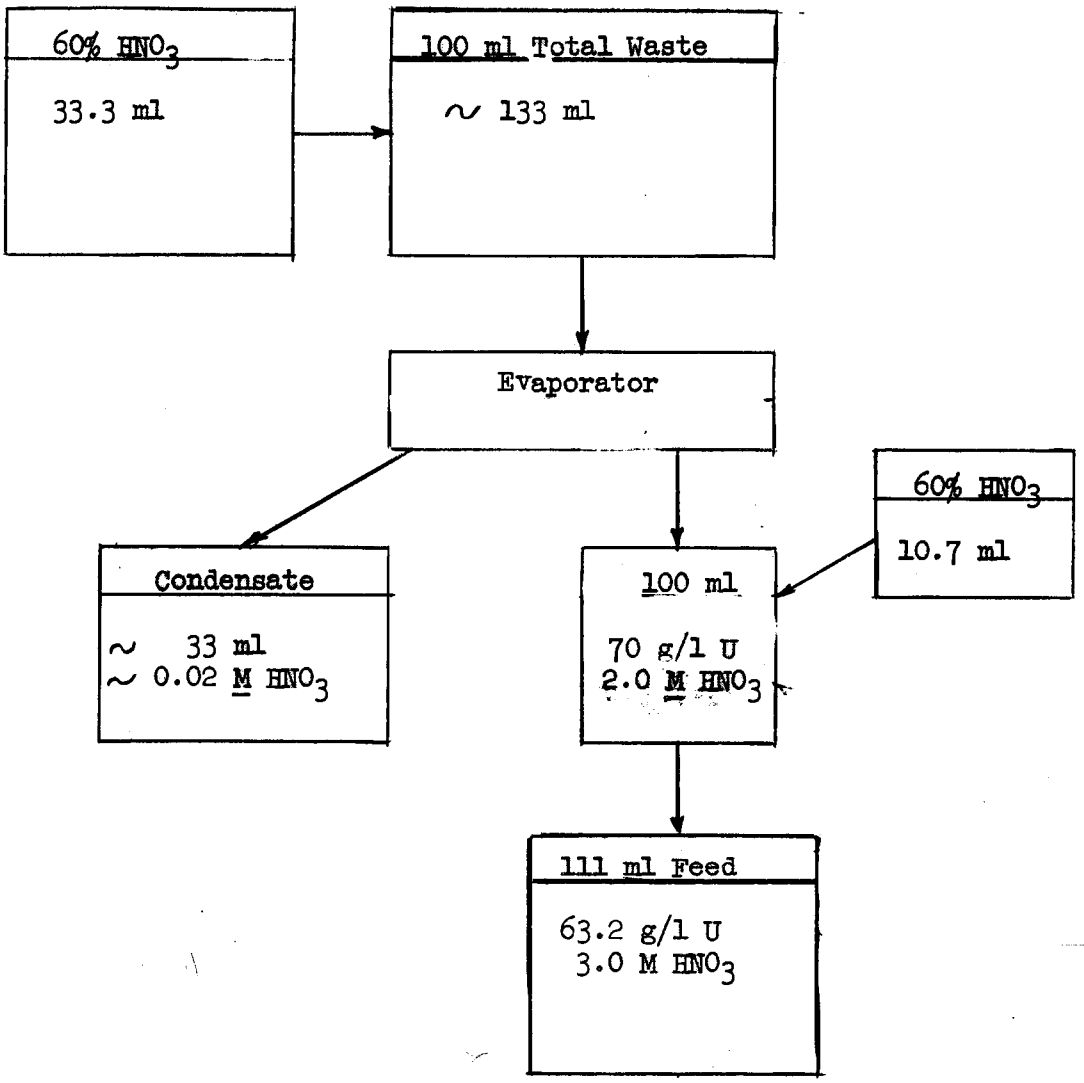


Figure 6

TBP Process Feed Preparation by HNO_3 Precipitation

Basis: 100 ml of Hanford supernatant (103U or 103T)

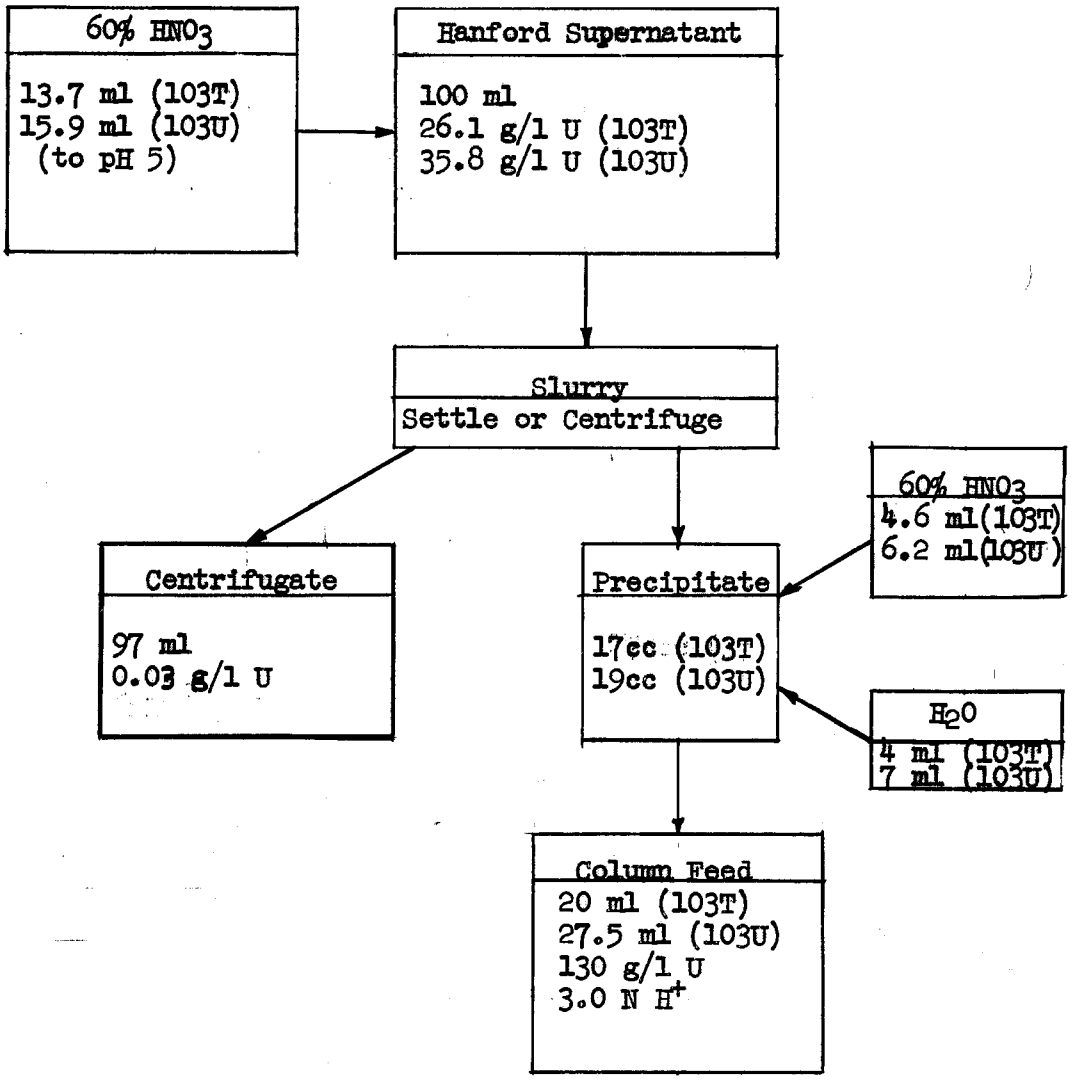


Figure 7

TBP PROCESS FEED PREPARATION BY HNO_3 PRECIPITATION

Basis: 100 ml of synthetic Hanford total waste
70 g/l U
(65 ml of Supernatant)
(35 ml of Sludge)

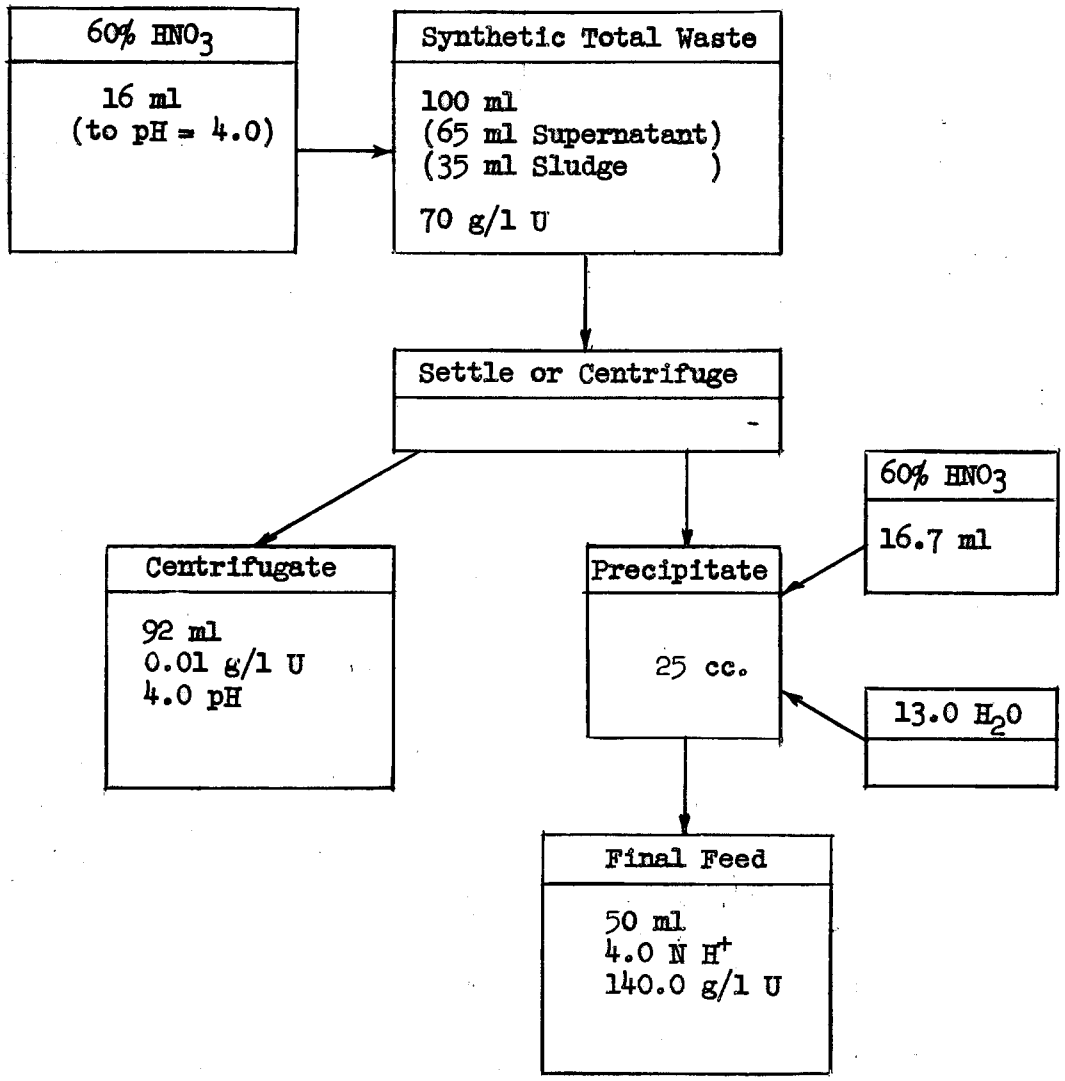
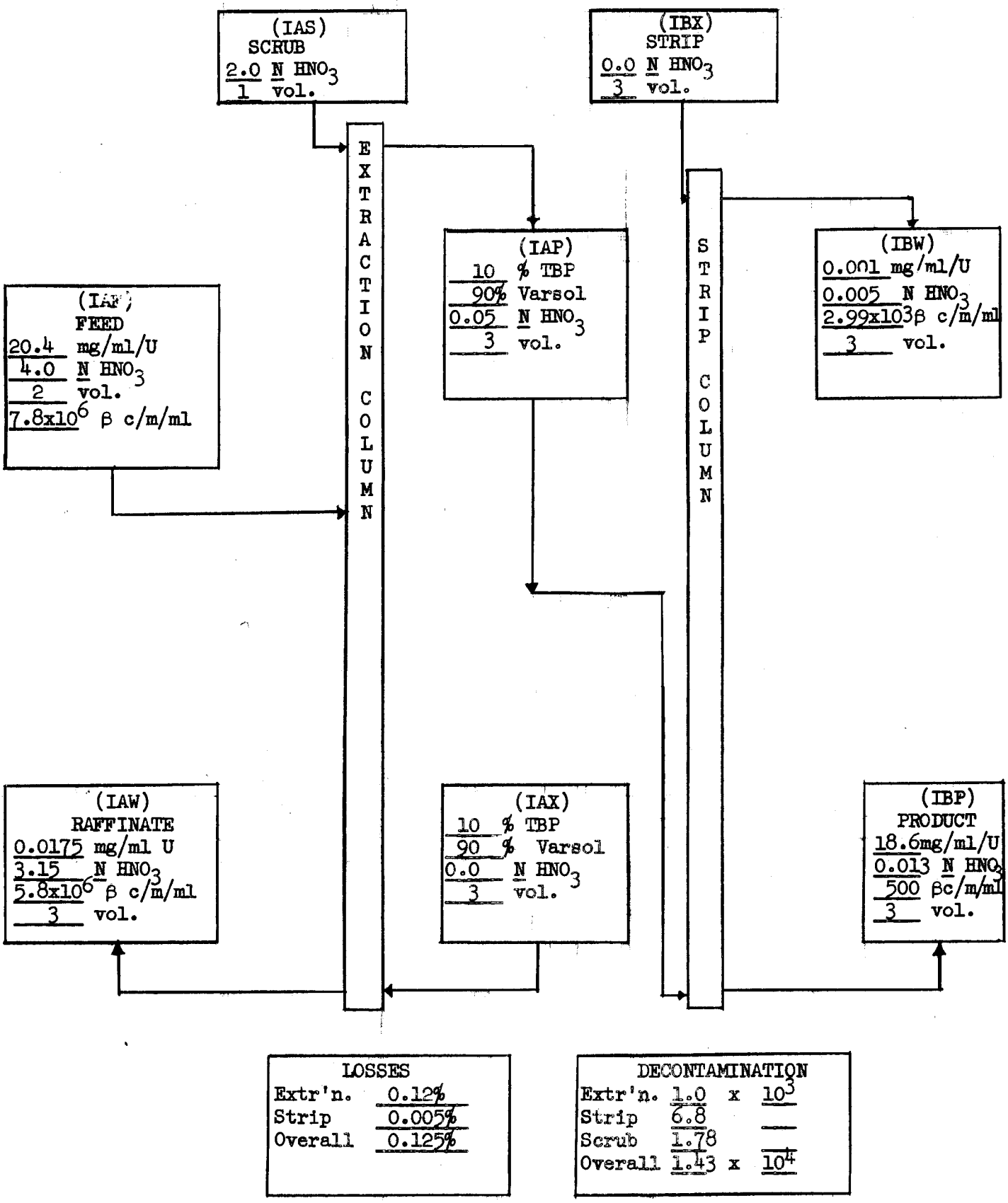


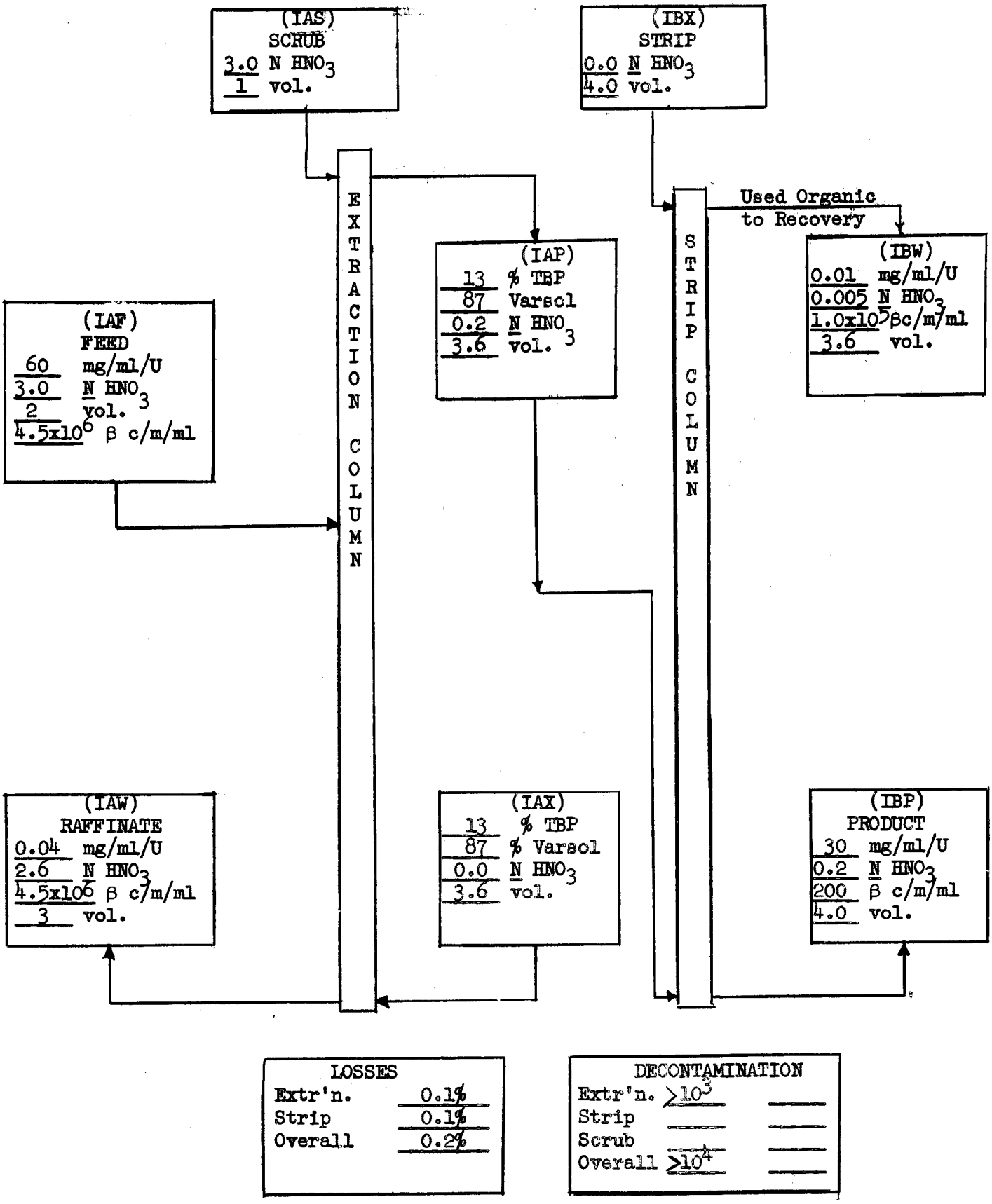
Figure VIII



SCHEMATIC FLOWSHEET

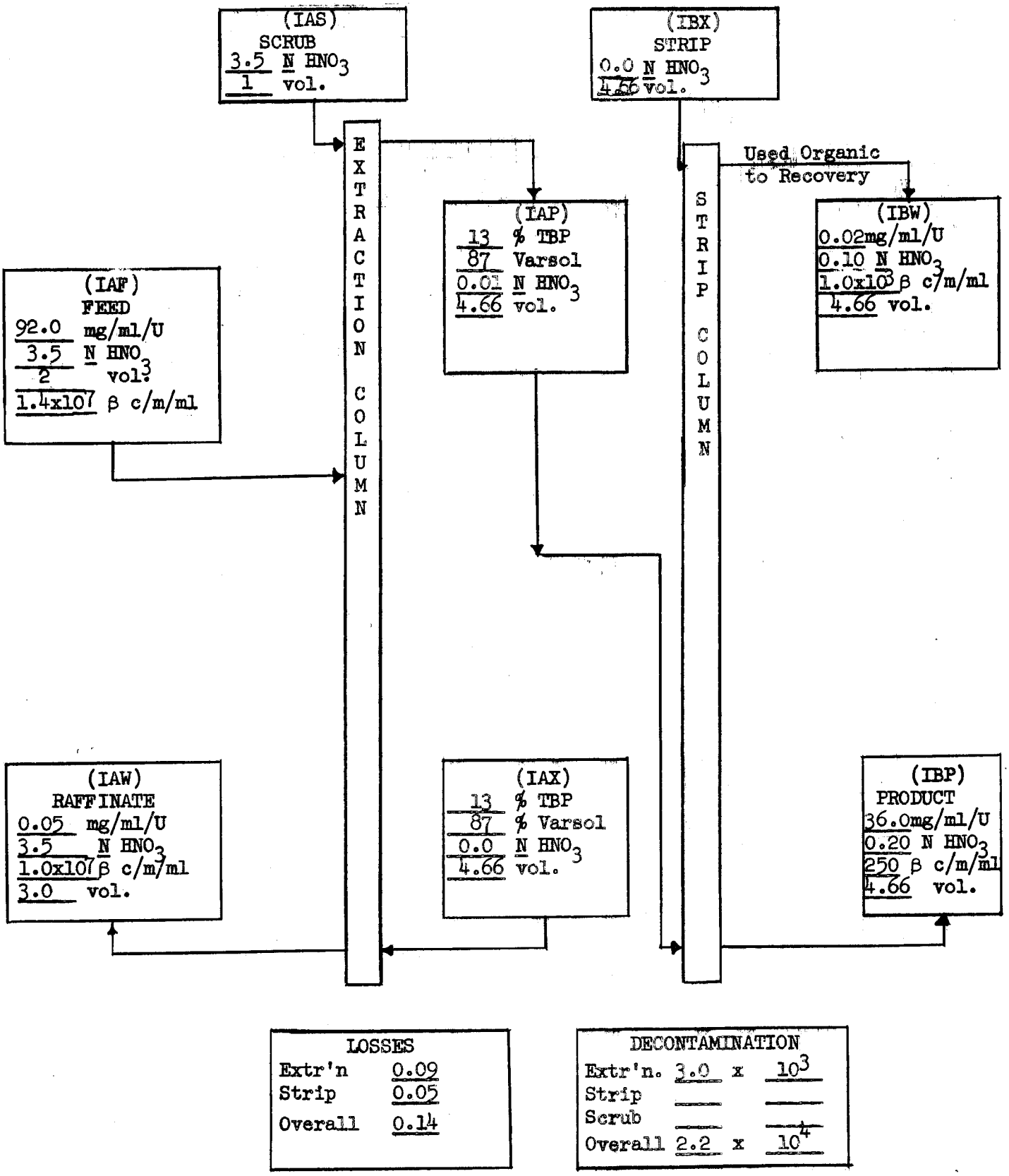
TBP PROCESS FOR URANIUM RECOVERY FROM METAL WASTE

Figure IX



SCHEMATIC FLOWSHEET
TBP PROCESS FOR URANIUM RECOVERY FROM METAL WASTE

Figure X



SCHEMATIC FLOWSHEET

TBP PROCESS FOR URANIUM RECOVERY FROM METAL WASTE

Figure XI

Average Variation of Uranium Dist. Coeff. with Stage Number in TBP Process

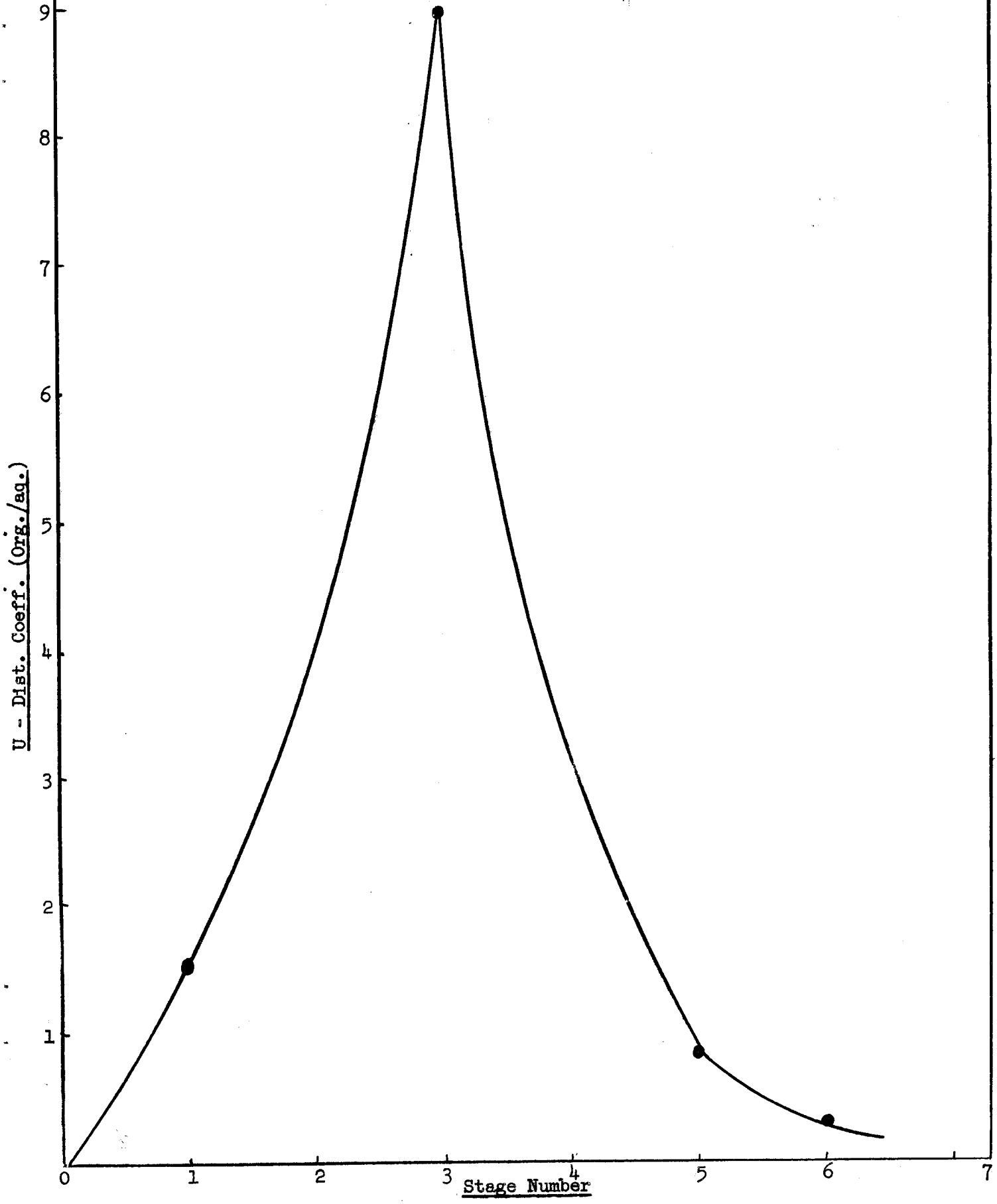
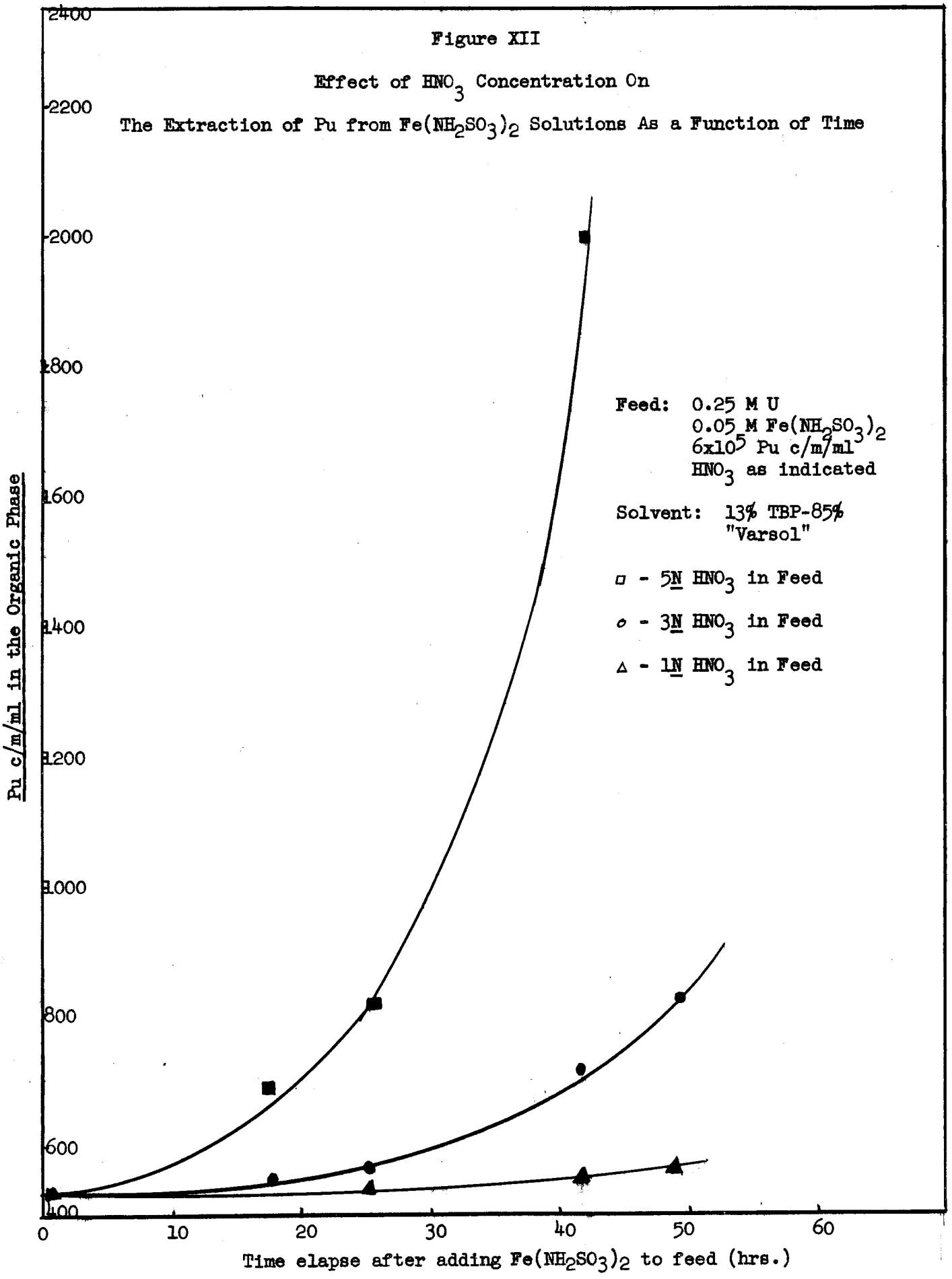


Figure XII

Effect of HNO_3 Concentration On

The Extraction of Pu from $Fe(NH_2SO_3)_2$ Solutions As a Function of Time



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8.5 Flooding-Rates In 1A and IB Columns for ORNL Wastes (10)

The flooding rate for the IA column was found to be 1000 gal/hr/ft.^{2} total through put. The flooding rate for the IB column was found to be 500 gal/hr/ft.^{2} total through put.

Flooding rates were determined in a 1-1/2 inch pyrex glass pipe column packed with 1/4 x 3/8 inch Raschig rings. The column was 10 feet in length containing about 9 feet of packed section. No scrub section was used, and the IAF and IAS were mixed before entering the column.

The flooding rate was taken as the rate of flow at which the packing no longer broke up the dispersed phase, or at which a second interface formed at the bottom of the column. For the IA column flooding was found to occur essentially at the same total through put for two flow ratios; solvent: aqueous phase = 1:1, and solvent: aqueous phase = 2:1. Only one flowratio was tested for the IB column; solvent: aqueous phase = 1:1.

8.6 HETS Determination for 1A Column Using ORNL Wastes (10)

Average HETS values for a 1-1/2 inch column 9 feet in length packed with 1/4 x 3/8 inch Raschig rings were: 75% of flooding - 3.6 feet, 50% of flooding - 3.0 feet and 25% of flooding - 2.5 feet. These values were determined from conventional XY diagrams of data determined in column runs and duplicate runs in the countercurrent batch extractor.

HETS determinations were made by the following method. Runs were made in a 1-1/2 inch column, 9 feet in height, packed with 1/4 x 3/8 inch Raschig rings and having four samplers set into the column in such a way as to permit

[redacted]

[redacted]

HETS Determination for 1A Column Using ORNL Wastes (continued)

sampling of the aqueous phase at four intermediate points of the column. Four such runs were made, one using ORNL sludge solution and three using a synthetic feed of approximate ORNL sludge solution composition.

With the synthetic feeds runs were made at 25%, 50% and 75% of flooding. The column was operated for more than three complete changes of the aqueous phase. Duplicate samples were taken for uranium analyses of the feed solution, of the aqueous phase at the four intermediate heights along the column, and of the aqueous raffinate. The run with ORNL sludge solution was made at about 60% of flooding, following the same procedure.

In connection with the column runs, similar feed solutions were processed in a four tube countercurrent batch extractor using the same flowratio that was used in the column. The tubes were sampled after three complete changes and the uranium concentration in both phases was determined.

Figure XIII shows a plot of the uranium concentration (g/l) in the aqueous phase as a function of distance from the feed plate (feet). The curve given was determined with synthetic ORNL sludge solution processed in the column at 50% of flooding.

The HETS values were found graphically in Figure XIII by plotting the concentration of uranium in the aqueous phase of each tube of the four stage countercurrent batch extractor made with identical conditions, determining where these concentrations intercept the uranium concentration line of the

[redacted]

[redacted]

HETS Determination for 1A Column Using ORNL Wastes (continued)

column, and scaling off the HETS from these intercepts.

The HETS for all four runs as determined by this method are given in Table 8.6-1.

[redacted]

[redacted]

Table 8.6-1

HETS For Tributyl Phosphate Extraction of Uranium from ORNL Wastes

Determined by Graphic Method Illustrated in Figure XIII.

Column: 1-1/2 inch Pyrex glass pipe, packed with 1/4 x 3/8 inch Raschig Rings about 9 feet of packing.

Solvent: 85% "varsol", 15% $(C_4H_9)_3PO_4$

Feed: Run #1 Mixture of one part of 3.0 N HNO_3 and two parts of HNO_3 solution of sludge from ORNL - W-10, 120 g/l - U, and 3.0 N acid.
Run #2, 3, 4: Mixture of one part of 3.0 N HNO_3 and two parts synthetic ORNL sludge solution; 3.0 N HNO_3, 1.0 N $NaNO_3$, 0.7 M $Na_2H\ PO_4$, 0.8 M Na_2SO_4 and 0.6 M UNH.

Run Code Number	Percent of flooding rate	Length of first stage (feet)	Length of second stage (feet)	Length of third stage (feet)
1	60%	2.0	2.5	4.5
2	75%	1.6	2.8	Less than 3 complete stages
3	50%	1.3	2.7	4.0
4	25%	1.3	2.7	3.6

[redacted]

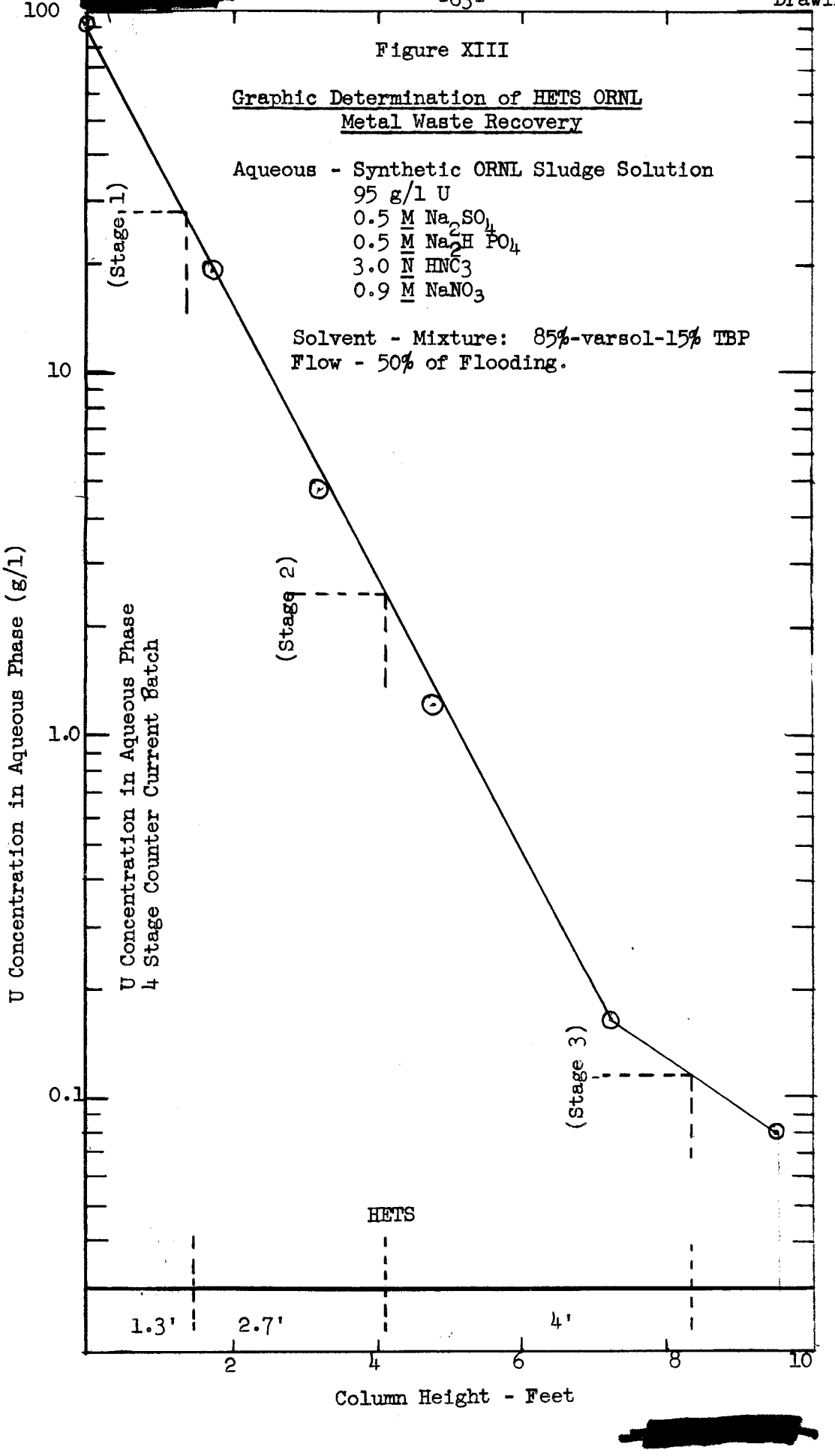
Drawing #8087

Figure XIII

Graphic Determination of HETS ORNL Metal Waste Recovery

Aqueous - Synthetic ORNL Sludge Solution
95 g/l U
0.5 M Na_2SO_4
0.5 M $Na_2H\ PO_4$
3.0 N HNO_3
0.9 M $NaNO_3$

Solvent - Mixture: 85%-varsol-15% TBP
Flow - 50% of Flooding.



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