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FURTHER STUDIES ON THE RECOVERY OF FISSION PRODUCTS

AND URANIUM FROM PUREX 1W

by

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I. INTRODUCTION

The recovery of fission products from Hanford wastes has for some time been under investigation by various HAPO workers. Flowsheets for the recovery of cesium have been demonstrated,¹ and one for the recovery of cerium is ready for full-level testing.² Several tentative flowsheets have also been proposed for the recovery of other fission products and of waste plutonium and uranium.^{3, 4, 5, 6} The "Integral Flowsheet" developed by Chemical Research Operation is based primarily on the work of G. B. Barton.^{3, 7}

The present work is a continuation of that begun by Barton.⁷ The primary objective has been the recovery of long lived fission products, other than cesium, with particular emphasis on cerium-144 and strontium-90. Secondary objectives of importance include: (1) the isolation of uranium and plutonium into solutions suitable for recovery by recycle into appropriate Purex plant streams, and (2) gathering data that may be useful at some later date on the recovery of the remaining fission products (other than cerium and strontium) should these become valuable. Precipitation procedures were principally considered since idle plant facilities already exist which were designed for this type of process. It is also desirable that the processes developed be compatible with the already demonstrated cesium recovery flowsheet.¹

II. SUMMARY

1. Data which can be applied to the development of flowsheets for the recovery of fission products and uranium from Purex LWV are presented. Included is the distribution of fission products between the hydrous ferric oxide precipitate (formed at low pH by gaseous ammonia neutralization of Purex LWV) and the supernatant liquid, and their path during subsequent operations aimed at isolating individual fission products.
2. Uranium. Over 90 percent of the uranium present in LWV remains in the supernatant liquid from the precipitation of iron at pH's up to 4.5. At pH 6, or above, greater than 90 percent of the uranium is lost to the precipitate. At pH 8, or above, uranium is quantitatively precipitated as the diuranate in the absence of complexing agents, but can be held in solution up to pH 9 with carbonate. At low pH (below 5) uranium can be precipitated with the iron if it is first reduced to the tetravalent state. Uranium is quantitatively precipitated at pH 2 by peroxide, in the absence of iron, with good separation from other activities, especially strontium.
3. Strontium. Greater than 90 percent of the fission product strontium will remain in solution during the precipitation of iron up to pH 6. Phosphate, iodate, or large concentrations of sulfate cause loss of strontium to the precipitate, however. Subsequent precipitation of uranium and the rare earths at pH 8 and 12 carry strontium to approximately 20 and 80 percent respectively. In the presence of small amounts of ferrous iron and phosphate (0.002 M), strontium is quantitatively carried at pH 9, or above. Fair separation from the rare earths and uranium is affected by precipitating strontium nitrate with fuming (90 percent) nitric acid, or by carbonate precipitation at pH 9.

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4. Cerium and the Rare Earths. These elements remain in solution during the precipitation of hydrous ferric oxide at low pH (≤ 3.0) provided the gross salt content of the solution is low. In the presence of sulfate concentrations above 0.3 M, phosphate above 0.004 M, or iron above 0.3 M, 30 to 90 percent of the cerium and rare earths are precipitated. All rare earths are quantitatively precipitated above pH 8.0 as hydroxides.
5. Zirconium and Niobium. These elements are removed from solution by the hydrous ferric oxide precipitate at low pH to an extent of about 90 percent. However, considerable variation was observed in the distribution from one experiment to another. Phosphate and manganese dioxide appear to precipitate these activities more completely and reproducibly.
6. Ruthenium. Ruthenium is carried on the hydrous ferric oxide precipitate to greater than 95 percent, and does not appear to offer any real problems to the proposed process.

III. EXPERIMENTAL

A. Solution Composition.

All experiments were run using the solution shown in Table III-1 as a stock solution. The solution is synthetic Purex 1WW based on Purex flowsheet HW No. 3.⁸

TABLE III-1

COMPOSITION OF SYNTHETIC PUREX 1WW

<u>Constituent</u>	<u>Molarity</u>
Nitrate	8.06
Hydrogen ion	7.55
Sodium	0.52
Sulfate	0.26
Iron (III)	0.15
Uranium	0.03

To this solution a spike of Purex plant 1WW was added (1 milliliter 1WW/liter of synthetic waste) to provide activity at a convenient level for analytical purposes. Individual fission products carriers were added as the need arose to the concentration shown in Table III-2.⁹ This simulates the fission product concentrations corresponding to the processing of 600 MWD/T, 5 MW/TU feed material, 90 day cooled, with final waste volume equal to 80 gallons per ton of uranium.

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TABLE III-2

CONCENTRATION OF FISSION PRODUCTS ADDED AS CARRIERS

<u>Fission Product</u>	<u>Concentration</u> <u>M X 10³</u>
Zirconium	2.69
Ruthenium	1.0
Strontium	0.86
Cerium	1.45
Niobium	0.09
Neodymium	1.56
Lanthanum	0.28
Yttrium	0.41

B. Techniques.

The initial precipitation of hydrous ferric oxide with ammonia was made after partially neutralizing with 50 percent sodium hydroxide to the incipient precipitation of iron (pH 0.5 to 1.5). The temperature of the solution at this point, due to the heat of reaction, was generally 80 to 90°C. This temperature was maintained by external heating, and an ammonia-air mixture was bubbled through the solution until the final pH was reached. This latter step required from one-half to four hours, depending on the rate of ammonia addition and the concentration of iron. Agitation was continued for one hour after the final pH was reached. Phase separation was effected by centrifugation. The pH of the solution was measured with a Beckman Model H-2 meter with calomel and glass electrodes. Agitation was supplied by magnetic stirring. Temperature was read by means of a thermocouple. This initial precipitation with caustic and ammonia will be referred to throughout the report as the Standard Procedure.

Zirconium-niobium, ruthenium, cerium, and cesium were usually determined by direct count on a gamma spectrometer. Chemical separations followed by appropriate counting were used as a check on the gamma spectrometer results, and for analyses of all other fission products and plutonium. Uranium results were obtained by fluorophotometer or X-ray analysis. The rare earth results represent the sum of the activities due to yttrium and the trivalent rare earths. A portion of the analytical control for the work was supplied by the Redox Analytical Laboratory and the remainder by the HLO Analytical Laboratories Operation. In isolated cases duplicate samples were supplied to both laboratories for methods verification. Fission product distribution is reported in the various tables as percent of the initial stock solution activity remaining at the stage under consideration. Unless

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otherwise noted, the analytical results are reported "as received" and have not been normalized. Consequently, mass balances are generally not 100 percent.

IV. DISCUSSION AND RESULTS

Those experiments which are applicable to a number of fission products are listed in tables found in the Appendix. These tables are referred to as the individual fission products are discussed in the following sections.

A. Precipitate Volumes.

The concentration of iron found in LWV varies over a considerable range. The maximum concentration reported from actual analysis is 0.8 M with an average for six analyses of 0.5 M.¹⁰ Unfortunately, this information was not available at the time the present work was done. Therefore, "flowsheet" concentrations of iron, and of other salts, were used in most of the experiments.

The hydrous ferric oxide precipitate volumes for a single iron concentration will vary considerably depending on conditions of the precipitation, precipitants, and gross salt concentration.¹¹ In Table IV-1 are listed the precipitate volumes found under various conditions.

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TABLE IV-1

HYDROUS FERRIC OXIDE PRECIPITATE VOLUMES

STOCK SOLUTION: Synthetic LWV with indicated dilutions and iron concentrations.

PROCEDURE: Standard procedure with indicated variation. The dilutions listed are the final volume (after neutralization) relative to initial LWV volume. The iron concentrations correspond to the final volume.

<u>Final pH</u>	<u>Fe(III) M</u>	<u>Dilution</u>	<u>Precipitant</u>	<u>Temp. °C</u>	<u>Precipitate Volume Percent*</u>
2.8	0.038	4	NaOH-NH ₃	80	1.8
1.5	0.079	2	NaOH-NH ₃	90	2.6
3.0	0.094	1.6	NaOH	80	10.0
2.7	0.085	1.7	NaOH-NH ₃	80	3.4
2.7	0.12	1.3	NaOH	90	9.4
3.0	0.12	1.3	NaOH-NH ₃	90	6.6
2.5	0.11	1.3	NaOH-NH ₃	80	5.2
2.8	0.16	4	NaOH-NH ₃	90	24
2.6	0.18	9	NaOH-NH ₃	90	27
4.0	0.44	4	NaOH-NH ₃	80	44

* Centrifuged precipitate volume as percent of final volume.

As was observed by Barton, the precipitates formed by gaseous ammonia precipitation are about a factor of two smaller than those formed with sodium hydroxide. The precipitate volumes listed for the higher iron concentrations (0.16, 0.18, and 0.44 M) are believed to be high by about a factor of two as compared to the results of H. H. Van Tuyl,¹¹ who has completed a more extensive investigation of the precipitates formed when LWV is neutralized.

B. Ruthenium, Zirconium, and Niobium.

Since the gamma spectrometer does not distinguish zirconium-95 from niobium-95, these activities are (except for isolated experiments) treated as a single activity throughout the investigation. The primary objective was to eliminate this activity from the product stream as early in the process as possible. A portion may be removed by filtering or centrifuging out the particulate matter which has been found in Purex LWV.¹ Some results showing the removal of zirconium-niobium from LWV by

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hydrous ferric oxide precipitation are shown in Table IV-2. These results, and those shown in Table VI-1 (Appendix), show a wide variation in the amounts of zirconium-niobium carried on the hydrous ferric oxide precipitate at low pH, with one to 20 percent generally remaining in solution. A few experiments were run in an effort to improve the carrying of zirconium-niobium. The addition of potassium permanganate to the acid waste (pH 0) with a heat kill to destroy the permanganate and precipitate manganese dioxide, followed by gaseous ammonia precipitation, improved zirconium-niobium carrying. The zirconium remaining in the supernatant liquid was 1.8 percent, and the zirconium-niobium content was not detectable on the gamma spectrometer. However, this method also causes loss of cerium to the precipitate, possibly because some of the cerium was oxidized to the (IV) state and is more readily carried than cerium (III). The addition of preformed manganese dioxide might eliminate this difficulty and should be tried.

The addition of phosphate (to a concentration of 0.004 M) to the acidic waste followed by the precipitation of iron gave similar results, due probably to the precipitation of zirconium phosphate. In fact, it is possible that there may be enough phosphate in plant LW (from hydrolysis of tributyl phosphate) to have this effect. If so, this would also affect the distribution of cerium and strontium since these elements too tend to be carried on ferric hydroxide in the presence of phosphate. Analytical data on the phosphate content of Purex plant LW is very meager. A sample taken on June 1, 1956 analyzed 0.003 M in phosphate; however, none could be detected in six samples taken more recently (detection limit 0.002 M).

Results for ruthenium were more consistent than for zirconium-niobium. From Table VI-1 it can be seen that ruthenium values in the supernatant liquid were not detectable in most cases. The lower detection limit of the gamma spectrometer is difficult to determine and depends on the amount of other activities present. However, in the presence of other reported activities, a "not detectable" result would represent less than one percent of the ruthenium activity initially in the stock solution.

Table IV-2 lists some experiments in which ruthenium chemical separations were made before counting. These results too show that 97 percent or more of the ruthenium will be carried on the hydrous ferric oxide precipitate.

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TABLE IV-2

RUTHENIUM AND ZIRCONIUM-NIOBIUM DISTRIBUTION BETWEEN THE SUPERNATANT LIQUID AND
THE HYDROUS FERRIC OXIDE PRECIPITATE FROM PARTIALLY NEUTRALIZED LWV AT LOW pH

STOCK SOLUTION: Synthetic LWV plus Purex LWV spike.

PROCEDURE: Standard procedure with indicated variations.

<u>pH</u>	<u>T°C</u>	<u>Precipitant</u>	<u>Ruthenium Sup. Liq. (Percent)</u>	<u>Zr-Nb Sup. Liq. (Percent)</u>	<u>Special Conditions</u>
2.7	80	NaOH	0.86	17.0	
2.5	80	NaOH-NH ₃	2.6	8.5	
2.7	80	NaOH-NH ₃	1.9	13.5	
2.7	50	NaOH-NH ₃	5.9 (102)*	15.0 (41)*	Ru, Zr, Ce, Nd, Sr, La carriers added.
2.8	80	NaOH	2.8	4.3	0.001 M Na ₂ S, 10 ⁻⁵ M Ru carrier.
2.8	80	NaOH-NH ₃	1.4	7.3	0.001 M Na ₂ S, 10 ⁻⁵ M Ru carrier.

* Numbers in parentheses are precipitate values obtained by analysis.

C. Uranium.

The chemistry of uranium is fairly well understood and its path in the proposed flowsheets can be predicted with confidence. However, since it is one of the constituents of Purex waste that has value, a number of experiments were run to verify its behavior under the specific conditions encountered.

Uranium can be readily controlled such that it can be precipitated or held in solution at will. The effect of pH on the removal of uranium is shown in Table VI-1 and Figure I. At pH 6, or above, uranium(VI) is precipitated as the diuranate. However, in the presence of excess carbonate, or of several other complexing agents, uranium is held in solution up to pH 9. This is shown by experiment 3, Table IV-3.

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TABLE IV-3

EFFECT OF REDUCTION AND CARBONATE COMPLEXING ON URANIUM DISTRIBUTION

STOCK SOLUTION: Synthetic LWV plus Purex LWV spike.

PROCEDURE: Standard Procedure with indicated variations.

<u>Exp. No.</u>	<u>pH</u>	<u>Precipitant</u>	<u>Percent U Sup. Liq.</u>	<u>Special Conditions</u>	<u>Fission Product Carriers Added</u>
1	4.5	NaOH-NH ₃	38.0	0.005 M NH ₂ OH	Ru, Zr, Ce, Sr.
2	4.5	NaOH-NH ₃	7.0	0.01 M NH ₂ OH	Ru, Zr, Ce, Sr, Nd, La.
3	9.0	NaOH-NaCO ₃	90.0		Ru, Zr, Ce, Sr, Nd, La.
4	4.5	NaOH-NH ₃	90.0	Control	Ru, Zr, Ce, Sr.

Below pH 4.5 uranium(VI) does not precipitate and is not carried on hydrous ferric oxide. However, if the uranium is reduced to the tetravalent state with hydroxylamine (Table IV-3, Exp. 1 and 2), it will precipitate with the iron.

After precipitating hydrous ferric oxide at pH 3.0, uranium can be precipitated from the supernatant solution by peroxide. The results of experiments with inactive solutions to establish conditions for the peroxide precipitation of uranium are shown in Table IV-4.

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TABLE IV-4

PRECIPITATION OF URANIUM AS THE PEROXIDE

STOCK SOLUTION: Synthetic LWV, no fission products added.

PROCEDURE: 1. NaOH added to pH 3, slurry centrifuged and precipitate discarded. Supernatant liquid adjusted to pH 8 and slurry centrifuged, supernatant liquid discarded. Precipitate dissolved in acid and adjusted to indicated pH. H_2O_2 added and slurry digested 60 minutes. Numbers represent the percent of uranium precipitated from final solution.

2. NaOH added to pH 3.0, slurry centrifuged and precipitate discarded. Supernatant liquid adjusted to indicated pH and H_2O_2 added. Slurry digested 60 minutes and centrifuged.

Exp. No.	Procedure	Initial pH	Final pH	Percent U ppt.	H_2O_2 M	Other Reagents
1	1	3.5	2.2	99.96	0.42	---
2	1	3.5	2.2	99.55	0.42	0.005 M Na_2S
3	1	3.5	1.4	99.67	0.42	---
4	2	3.0	2.0	69.10	0.10	---
5	2	3.0	2.0	95.90	0.30	---
6	2	3.0	2.0	99.38	0.90	---
7	1	3.0	3.0	94.80	0.10	---

In procedure 1, the removal of the gross salts by precipitating the diuranate at pH 8 aids considerably in the subsequent removal of uranium with peroxide. However, greater than 99 percent of the uranium can be precipitated with the gross salts present if sufficient excess peroxide is used (Exp. 6, Table IV-4). Due to the shortage of time, the procedure received only limited testing with radioactive solutions. The results are shown in Tables VI-4, and VI-5. Rather poor carrying of uranium resulted in Table VI-5 due, probably, to the high sodium nitrate concentration (ca. 10 M). In Table VI-4 there was good carrying of uranium, but very poor separation from cerium. More work would need to be done on this system to optimize conditions. Neither of the precipitations in Tables VI-4 and VI-5 are considered optimum.

D. Strontium.

In the absence of high concentrations of sulfate, iodate, and phosphate, strontium remains for the most part in solution during the precipitation of iron with ammonia (Table VI-1). In one experiment, the addition of peroxydisulfate to 0.05 M (bringing the sulfate concentration of the final solution to about 0.30 M) caused a loss

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of about 40 percent of the strontium to the precipitate. It has also been demonstrated that the precipitation of ceric and rare earth sulfates from 1WW, at pH's below the point where iron precipitates, carries 25 to 35 percent of the strontium.² Iodate also carries about 30 percent of the strontium under similar conditions. G. B. Barton demonstrated that ferric hydroxide at pH 11, or above, would carry 99 to 100 percent of the strontium.⁷ At pH 8, in the absence of iron, the diuranate and rare earth hydroxide precipitates carry about 20 percent of the strontium. Small amounts of phosphate and ferrous iron (0.002 M) at pH 9 cause quantitative precipitation of the strontium (procedure 2, Table VI-4).

An effort was also made to isolate strontium from solution, after the removal of iron, by precipitation of strontium nitrate from fuming nitric acid (Table VI-3). Fair yields were obtained with good separation from other elements. However, fuming nitric acid (80 to 90 percent) is a highly corrosive reagent and would be difficult and expensive to use in large quantities. Therefore, a more practical approach might be to precipitate the uranium and the cerium away from the strontium as the peroxide and iodate respectively. Some of the other carriers investigated by Barton,⁷ i.e. barium and calcium carbonates, may also be effective substitutes for fuming nitric acid. In one experiment using carbonate alone at pH 9, only 13 percent of the strontium was found in the supernatant liquid.

E. Cerium and the Rare Earths.

Cerium may prove to be a very valuable fission product. It has a relatively long half-life of 285 days coupled with an energetic beta of nearly 3 MEV. These facts make its use as a heat source for certain specialized applications very attractive.¹³

The effect of pH on cerium is shown in Table VI-1. Cerium loss to the hydrous ferric oxide precipitate begins to rise at pH 4.5 and increases rapidly above this pH. At pH 8.0 (Table VI-5) the cerium is quantitatively precipitated even in the absence of iron. Early in the investigation, results indicated that large amounts (30 to 60 percent) of the cerium would be lost to the hydrous ferric oxide precipitate at pH 3.0. As a result, experiments were run designed to shift the cerium distribution so that at least a nine to one split could be obtained, the larger fraction preferably shifted to the supernatant liquid. In Table IV-5 are listed some of the earlier results (Exp. Nos. 1, 2, 3, 4 and 5) and those techniques which were employed to shift the cerium either to the supernatant liquid or the precipitate.

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TABLE IV-5

CERIUM DISTRIBUTION BETWEEN THE HYDROUS FERRIC OXIDE PRECIPITATE
AND THE SUPERNATANT LIQUID UNDER VARIOUS CONDITIONS

STOCK SOLUTION: Synthetic LWV plus Purex LWV tracer.

PROCEDURE: Standard procedure with indicated variation. The dilution factor represents the final volume after all reagents have been added.

Exp. No.	pH	Temp. °C	Dilution Factor	Cerium Percent		Special Conditions
				Sup. Liq.	ppt.	
1	2.7	80	1.4	65	--	Sodium hydroxide only to final pH.
2	4.5	80	2.0	36	--	Sodium hydroxide only to final pH.
3	2.5	80	1.5	74	--	Standard procedure.
4	4.5	80	1.3	24	--	Standard procedure.
5	2.8	70	1.3	106	--	Standard procedure.
6	2.9	70	1.6	11	97	S ₂ O ₈ ²⁻ to 0.05 M.
7	4.5	90	1.4	52	--	NH ₂ OH to 0.01 M.
8	4.7	80	1.5	4	--	KIO ₄ to 0.01 M.
9	3.0	80	2.0	94.3	7.1	Fe(III) precipitated in 2 steps at pH 2.3 and 3.0.

Fission products carriers Ru, Zr, Ce, and Sr were added to all experiments except 1 and 3.

The results for the initial experiments 1, 3, and 5 show that from 65 to 100 percent of the cerium remains in solution at low pH. At a pH of 4.5, 50 to 75 percent loss to the precipitate was observed. The use of a reducing agent (Exp. 7) had no noticeable effect. Periodate at 0.01 M precipitated the cerium completely, presumably as ceric iodate or ceric hydroxide. More recent work on cerium recovery from Purex LWV² has established that sulfate concentrations above 0.60 M will also precipitate 80 to 95 percent of the cerium from partially neutralized LWV at pH's below the point at which iron precipitates. At the higher pH's where iron precipitates, one would expect that a lower concentration of sulfate would cause considerable loss of cerium to the precipitate. In Exp. 6, Table IV-5, peroxydisulfate (0.05 M) precipitated the cerium completely. This may be due either to excess sulfate or to the precipitation of ceric hydroxide.

In Exp. 9, the dilution of the gross salt content by a factor of two combined with the stepwise precipitation of iron appears to provide a method for precipitating the iron while leaving the cerium in solution. Table VI-2 also shows the effect of diluting the waste and the effect of various iron concentrations. The data shows

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that 0.19 M iron can be precipitated and still leave the cerium in solution if the waste is dilute enough. Iron concentrations of 0.4 M, however, appear to be too high even when precipitated stepwise. In actual practice, according to some recent analyses of Purex 1WW,¹² considerable dilution of the waste would have to be made in order to reach concentrations of sulfate and iron that would allow the precipitation of hydrous ferric oxide and still leave cerium and the rare earths in solution. In Table IV-6 the concentrations of constituents in the synthetic waste at a dilution of 1.5 are compared to actual Purex 1WW at dilutions of 1.5 and 3.0. It can be readily seen that minimum dilutions of a factor of three will be necessary to reach desirable concentrations of sulfate and iron.

TABLE IV-6

APPROXIMATE COMPOSITION OF PARTIALLY NEUTRALIZED PUREX 1WW COMPARED
TO SYNTHETIC 1WW (FLOWSHEET HW-NO. 3)

Concentrations expressed in molarity. pH of solutions about 1.5.

Constituent	Synthetic 1WW	Purex 1WW (average of six analysis)	
	Dilution 1.5*	Dilution 1.5*	Dilution 3.0
Nitrate	5.37	6.4	3.2
Sodium	5.41	5.93	2.97
Sulfate	0.17	0.67	0.33
Iron	0.10	0.33	0.16
Uranium	0.02	0.007	0.0035

* A dilution of 1.5 will normally occur during neutralization provided there is no evaporation

The removal of cerium prior to the precipitation of hydrous ferric oxide may actually be a better approach to the problem of cerium recovery, particularly if cerium only is desired. A flowsheet demonstrating the precipitation of cerium from 1WW as a sulfate has been prepared.²

V. PROCESS PROPOSALS

A number of flowsheets might be proposed based on the above results. The more attractive possibilities are presented stepwise below.

1. Dilute Purex 1WW by a factor of four and neutralize to the incipient precipitation of iron with 50 percent sodium hydroxide. Temperature at this point will be 90 to 100°C.

2. Bubble gaseous ammonia through the solution at 90°C to a pH of 2.0, centrifuge out the iron precipitate, and add ammonia again to the final pH of 3.0. Digest one hour or more and centrifuge out the remaining iron. (Although it has not

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been investigated, the continuous centrifugation of the hydrous ferric oxide precipitate as it is formed may be a better method, providing ruthenium and zirconium-niobium activities are still carried satisfactorily.)

3. The supernatant liquid from step 2 should contain the uranium, strontium, cesium, cerium, the rare earths, and most of the plutonium. The precipitate will contain the zirconium, niobium, and ruthenium and may be stored or further processed to recover these activities.

4. Take the supernatant liquid to pH 10 and add phosphate and ferrous iron to 0.002 M. Separate phases by centrifugation. The supernatant liquid containing the gross salts from LW and fission product cesium may then be processed by the flowsheet developed by Van Tuyl¹ for cesium isolation.

5. Dissolve the precipitate from step 4 (containing the strontium, uranium, cerium, and the rare earths), in a minimum volume of acid. Reduce the uranium to the (IV) state with hydroxylamine and precipitate at pH 4.5 with the iron. The iron and uranium can be easily separated by dissolving the precipitate, oxidizing the iron and uranium and precipitating the iron at pH 3.0 as in step 1 above. (An alternate method would be to remove the iron by precipitation at low pH, then separate the uranium from the fission products by peroxide precipitation.) Acidify the supernatant liquid from the uranium-iron precipitation to 1.5 M nitric acid, and oxidize the cerium to the tetravalent state and precipitate as ceric iodate.² Subsequent handling of the ceric iodate precipitate is covered in another report.²

6. Evaporate the supernatant liquid from the iodate precipitation (containing the rare earths and strontium) to low volume and take up in fuming (90 percent nitric acid). This precipitates the strontium as the nitrate leaving the rare earths in solution.

The path of plutonium past the first precipitation is not shown due to the lack of data. From the chemistry of plutonium, however, one would predict that it would follow the uranium under the conditions described.

Subsequent purification of the various fission products has not been studied, nor has any of the steps shown above been as thoroughly checked as they should be prior to plant application. Larger scale testing of the procedures shown above would be the next logical step in the development of firm and workable flowsheets for the recovery of fission products from Purex waste.

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VI. APPENDIX

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FIGURE 1

FISSION PRODUCT AND URANIUM DISTRIBUTION BETWEEN
THE HYDROUS FERRIC OXIDE PRECIPITATE FROM
NEUTRALIZED PUREX IWW AND THE SUPERNATANT LIQUID-EFFECT
OF pH.

TABLE VI-1

EFFECT OF pH ON FISSION PRODUCT DISTRIBUTION BETWEEN THE HYDROUS FERRIC OXIDE

PRECIPITATE AND SUPERNATANT LIQUID

STOCK SOLUTION: Synthetic LMW spiked with Purex LMW to 0.1 percent full level.

PROCEDURE: Fission product carriers* added to stock solution and digested ten minutes, sodium hydroxide added to pH 1.0, ammonia-air to final pH (70 to 90°C). Digested 60 minutes, centrifuged, precipitate washed once. Numbers represent percent of initial element remaining in supernatant liquid. Neutralization and reagent addition causes dilution by a factor of 1.5.

Exp. No.	pH	Percent in Sup. Liq.							Special Conditions
		Zr-Nb	Ru	Cs	Ce	RE-Y	SR	U	
1	1.5	ND	ND	100.0	98.5	98.8	98.8	99.0	99.0
2	2.0	14.2	ND	47.0 (?)	83.0	72.0	91.0	106.0	--
3	2.7	9.1	ND	100.0	87.5	94.0	100.0	100.0	86.0
4	3.2	7.5	ND	24.0 (?)	92.0	101.0	93.0	94.0	--
5	3.5	0.8	1.2	101.0	99.0	100.0	113.0	100.0	--
6	4.5	8.9	ND	81.0	72.0	--	91.0	38.0	--
7	4.5	12.9	ND	54.0	51.0	--	81.0	93.0	--
8	4.5	28.0	ND	85.0	34.0	87.0	87.0	101.0	--
9	6.0	14.4	ND	86.0	63.0	50.0	93.0	8.9	--
10	6.0	32.0	3.5	80.0	48.0	--	84.0	5.1	--

Hydroxylamine added to 0.005 M to acid waste.

Duplicate sample analyzed by another laboratory.

* Experiments 1 and 3 contained fission product carriers to the following concentrations. M X 10³: Sr 0.86, Cs 1.45, Ce 0.53, Nd 1.56, Zr 2.69, Nb 0.09, Y 0.41, Ru 1.0. Remaining experiments contained only Zr, Ru, Ce, and Sr to concentrations given in Table III-2. See also Figure I.

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TABLE VI-2

EFFECT OF GROSS SALT CONTENT AND OF IRON (III) CONCENTRATION ON THE DISTRIBUTION
OF FISSION PRODUCTS AND URANIUM

STOCK SOLUTION: Synthetic LW plus Purex LW spikes to 0.1 percent full level.

PROCEDURE: Standard procedure with indicated variations. Iron concentration was varied by addition or dilution and gross salt content by dilution. Fission product carriers Zr, Ru, Ce, Cs, Sr, Nd, and Nb were added to concentrations given in Table III-2. Percentages are rounded to whole numbers.

Exp. No.	pH	Dilution Factor	Fe(III) M	Ruthenium		Zr-Nb		Cerium**		Cerium		RE-Y		Uranium		Strontium		Plutonium		Remarks
				SL	ppt.	SL	ppt.	SL	ppt.	SL	ppt.	SL	ppt.	SL	ppt.	SL	ppt.	SL	ppt.	
1	3.4	1.5	0.10	ND	96	20	82	23	68	21	72	79	39	94	10	85	27	-	-	Control
2	2.7	1.6	0.094	ND	98	7	71	70	10	72	14	113	7	93	--	104	ND	112	18	(1)
3	3.0	2.0	0.075	ND	69	--	--	88	7	94	7	--	--	113	--	76	--	84	--	(2)
4	2.8	4.0	0.038	ND	51	ND	61	77	9	52	12	94	7	88	--	101	--	74	14	
5	3.0	4.0	0.15	ND	116	ND	54	80	12	126	21	87	13	--	--	122	--	77	11	
6	4.0	4.0	0.40	ND	99	ND	69	47	37	83	46	64	18	--	--	91	--	46	13	(3)
7	2.6	9.0	0.19	ND	--	ND	71	89	26	120	27	79	24	74	0.01	108	ND	69	21	

* SL represents supernatant liquid.

ND Not detectable.

** Cerium by gamma spectrometer, other cerium results by beta counting after radio-chemical separation.

(1) Sample initially neutralized to pH 3.5 then adjusted to final pH.

(2) Stepwise precipitation of iron at pH 2.3 and finally at 3.0.

(3) Stepwise precipitation of iron at 6 successively higher pH's finally ending at pH 4.0.

-- Result not available or obviously erroneous.

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TABLE VI-3

ISOLATION OF STRONTIUM BY PRECIPITATION FROM NINETY PERCENT NITRIC ACID

STOCK SOLUTION: Synthetic LWV plus Purex LWV spike to 0.1 percent full level.

PROCEDURES:

1. Sr carrier added to 8.6×10^{-4} M, NaOH-NH₃ at 80°C to pH 2.7, centrifuged, precipitate discarded. Supernatant liquid sampled (A).
2. Supernatant liquid from 1 adjusted to pH 12.0 with NaOH, centrifuged supernatant liquid sampled (B).
3. Precipitate from 2 dissolved in 90 percent nitric acid, centrifuged, supernatant liquid sampled (C). Precipitate dissolved in water (D).

<u>Sample No.</u>	<u>Zr-Nb</u>	<u>Ruthenium</u>	<u>Cesium</u>	<u>Cerium</u>	<u>Strontium</u>	<u>Uranium</u>	<u>Sample Description</u>
A	13.5	1.9	96	106	104	101	Supernatant liquid from pH 2.7.
B	-	-	-	-	19	-	Supernatant liquid from pH 12.6.
C	4.2	2.4	-	48	17	58	90 percent nitric acid supernatant liquid.
D	0.8	-	-	4.6	70	-	90 percent nitric acid precipitate.

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TABLE VI-4

ISOLATION OF URANIUM FROM PUREX LWV AS THE PEROXIDE

STOCK SOLUTION: Synthetic LWV plus Purex LWV to 0.1 percent full level.

PROCEDURES:

1. Sr carrier added to 3.9×10^{-4} M, NaOH-NH₃ added to pH 3.5, centrifuged. Precipitate discarded. Supernatant liquid sampled as (A).
2. Supernatant liquid (A) adjusted to pH 10, disodium phosphate added to 0.002 M and Fe (II) added to 0.0013 M, slurry stirred 20 minutes and centrifuged. Supernatant liquid sampled as (B).
3. Precipitate from 2 dissolved in nitric acid and pH adjusted to 3.5, stirred 20 minutes, and centrifuged. Precipitate discarded. Supernatant liquid sampled (C).
4. Supernatant liquid (C) made 0.08 M in peroxide, digested 20 minutes, and centrifuged.

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Sample No.	pH	Zr-Nb	Ruthenium	Cesium	Cerium	RE-Y	Strontium	Uranium	Sample Description
A	3.5	0.8	1.2	101	99	100	113	105	Sup. liq. from pH 3.5 precipitation.
B	10	-	-	-	-	-	0.5	7.8	Sup. liq. from pH 10.0 precipitation.
C	3.5	-	-	-	-	-	104	108	Sup. liq. from 2nd low pH (3.5) precipitation.
D	4.8	0.08	ND	5.6	54	72	93	3.2	Sup. liq. from peroxide precipitation.
E	-	0.45	ND	2.9	36	13	5.1	88.5	Dissolved peroxide precipitate.

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TABLE VI-5

ISOLATION OF URANIUM FROM PUREX 1W

STOCK SOLUTION: Synthetic 1W plus Purex 1W to 0.1 percent full level.

PROCEDURES:

1. Carrier Zr, Ce, Ru, and Sr added to stock solution, NaOH-NH₃ at 80°C to pH 3, slurry digested 30 minutes and centrifuged. Precipitate washed and discarded. The wash solution and supernatant liquid were combined and sampled (A).
2. Ammonia added to the supernatant liquid (A) to pH 8, digested 30 minutes, and centrifuged. Supernatant liquid sampled (B).
3. Precipitate from 2 treated with 90 percent nitric acid, and centrifuged. Precipitate dissolved in water (C). Supernatant liquid sampled (D).
4. Supernatant liquid from 3 neutralized to pH 3 and H₂O₂ added to 0.12 M, slurry digested 30 minutes and centrifuged. Supernatant liquid (E). Precipitate dissolved in acid (F).

Sample No.	Zr-Nb	Ruthenium	Cerium	Strontium	Uranium	Sample Description
A	23	4.7	100	86	107	Supernatant liquid from pH 3 precipitation.
B	ND	0.08	0.2	71	-	Supernatant liquid from pH 8.0 precipitation.
C	-	-	1.3	85	-	Precipitate from 90 percent nitric acid.
D	-	-	64	11	128	Supernatant liquid from 90 percent nitric acid.
E	21	-	67	-	37	Supernatant liquid from peroxide precipitation.
F	1.2	-	0.6	-	37	Dissolved peroxide precipitate.

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