TRIBUTYL PHOSPHATE-HYDROCARBON DILUENT

REPURIFICATION IN RADIOCHEMICAL PROCESSING

AT ORNL: STATUS SUMMARY

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OAK RIDGE NATIONAL LABORATORY
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Tributyl Phosphate-Hydrocarbon Diluent Repurification in
Radiochemical Processing at ORNL: Status Summary

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ABSTRACT

The need for, and the adequacy of, the sodium carbonate washing technique in chemical purification of tributyl phosphate--hydrocarbon extractant prior to its re-use in radiochemical processing was examined, primarily in terms of ruthenium, zirconium, and niobium activities. Although it is emphasized that these radiation activities may not be the best, or even a very good, measure of solvent quality, they form the only measure now in extensive enough use to permit interplant comparisons. Hanford operating experience has shown that if the combined ruthenium, zirconium, and niobium gamma activities in the first cycle extractant (30% TBP in kerosene diluent) exceed 4-5 mcuries per gallon of extractant, the zirconium activity in the plutonium product from the plant starts to exceed specifications. For this reason the value 4-5 mcuries (Ru+Zr+Nb)/gallon was chosen as a reference point to fix the maximum allowable value of the sum of these activities in the 1AX stream. No similar reference for activity in second cycle solvent is available. On this basis, purification of the 1CW used solvent stream of the ORNL Purex Pilot Plant was on the borderline of being necessary, and it was adequate; activities in used and recovered second cycle solvent from the ORNL Purex Pilot Plant were lower than corresponding Hanford values. Purification of contaminated solvent from the first cycle raffinate prior to use in the second cycle in the ORNL Thorex Pilot Plant long-decay runs was probably necessary and was adequate if Hanford second cycle activity data are used as a reference. However, in Thorex short-decay runs, decontaminated first cycle solvent contained about 100 times as much activity as second cycle solvent at Hanford. Thus, although this solvent was adequately decontaminated for re-use in the first cycle, it was probably much too contaminated for use in the second cycle of Thorex short-decay operations.

Although there are differences in the sodium carbonate-aqueous purification systems at Hanford and ORNL, all systems give ruthenium-zirconium-niobium total decontamination factors of 10 for first cycle solvent and of 2-6 for second cycle solvent. The wide variation in solvent decontamination at ORNL, especially during Thorex operations, was probably due largely to entrained solids, and to a small extent to entrained aqueous phase. Data from the various plants led to the following suggested upper limits for activity in solvent fed to the first and second cycles of any TBP-based processes: first cycle, 2 mcurie/gal, which is a well-defined reference; second cycle, 0.03 mcurie/gal, which is a poorly defined, and possibly unnecessarily low, reference. It is recommended that the ORNL Power Reactor Fuel Processing Pilot Plant be used in development studies to determine: (1) the mechanism and extent of the decontamination achieved by sodium carbonate solutions; (2) the adequacy of retained fission product activity as a measure of solvent purity; (3) methods of removing solids from used solvent; and (4) the establishment of TBP-diluent specifications and use tests.

CONTENTS

1.0 INTRODUCTION

This report evaluates solvent recovery operations in the ORNL Thorex Pilot Plant in terms of decontamination of product and solvent streams and of laboratory data on TBP decomposition and repurification. The evaluation is made with reference knowledge that the Hanford Purex process is working very well and that the activity of TBP-hydrocarbon solution from the solvent recovery system, which is recycled to the uranium and plutonium recovery equipment, is 1-3 mcuries/gal.[9] Brief mention is also made of use of "as received" TBP, whose impurity content is unknown.

Tributyl phosphate (TBP) in a hydrocarbon diluent is extensively used in solvent extraction processes for separating fissile or fertile elements, e.g., uranium, thorium, and plutonium, from both radioactive and nonradioactive impurities. The TBP suffers a small amount of dealkylation* due to reaction with aqueous nitric acid, which may be present to the extent of several moles per liter, and radiation decomposition. Degradation products include dibutyl phosphoric acid, monobutyl phosphoric acid, orthophosphoric acid, polymeric materials, unsaturated hydrocarbons, and unidentified nitrogen-containing organic compounds. These substances cause loss of uranium, probably loss of plutonium and thorium, and lowered decontamination from certain fission products. To decrease the buildup of degradation products the solvent-diluent solution is processed through a recovery system. This system usually contains one or more units for contacting the solvent with aqueous sodium carbonate and/or sodium or potassium hydroxide solution to remove the acid degradation products. Various units, including centrifuges, sand filters, and hydroclones, have been used in efforts to remove solids.

Numerous laboratory studies of the acid-induced dealkylation and radiation-induced decomposition of TBP have been published (see references 5 and 29 for summaries). So, also, have been studies of the amount of decontamination of TBP-diluent solutions, with respect to various quantities of fission product elements, as a result of treatment with aqueous solutions of sodium carbonate, sodium hydroxide, calcium hydroxide, etc.[12,14,17,19,20,23] However, with few exceptions, these data have not been applied to operating solvent extraction systems. Specifically, factors such as the following have not been evaluated: (a) loss of uranium in a first cycle waste due to aqueous solubility of uranyl monobutyl phosphate vs. total uranium loss in the stream; (b) effect of degree of contamination of solvent with radioactive nuclides on the degree of decontamination of the product streams. Such evaluations are needed because extractant decomposition products are not the only sources of loss of valuable elements or reduced decontamination.

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*In acidic solution TBP probably undergoes dealkylation as does trimethyl phosphate, corresponding to cleavage of the C-O bond in the C-O-P grouping; in alkaline solution, hydrolysis corresponding to cleavage of the O-P bond in the C-O-P grouping occurs.[3]

The amount of retained radioactivity is used in this report as a measure of the adequacy of solvent recovery processes because no other measure has yet been used very extensively. It should be emphasized that we do not at present know how good this type of measure is.

In writing this summary of information on solvent recovery at ORNL, the author has been aided by valuable discussions with many members of the Laboratory. Particular thanks are due W. T. McDuffee, E. M. Shank, and R. H. Rainey. Also acknowledged is the help of J. R. Parrott, A. T. Gresky, E. D. Arnold, J. R. Flanary, and R. E. Blanco of the ORNL Chemical Technology Division and S. A. Reynolds of the ORNL Analytical Chemistry Division.

2.0 SOLVENT RECOVERY

Data presented below are primarily from runs HD-16 through HD-27 and SD-1 through SD-3 of the Thorex Pilot Plant. These runs were chosen for study because they represent a relatively long series in which the specific activity of feeds and contaminated solvent varied by a factor of 10^4. They were of relatively short duration, varying from a few days to a few weeks in length.[18]

2.1 Sampling and Analyses

Samples of solvent for radiochemical analyses were obtained by use of a sampling unit described by Duggan and Landry.[10] Use of this sampler provided samples that were representative of the holdup tank or flowing stream in question up to, and including, entrained aqueous phase and solids. Most of the samples discussed below were taken from: (1) the T-4 holdup tank upstream from a (T-1) pulsed-column sodium carbonate solution contactor; (2) an expanded section of piping in the organic discharge line downstream from the T-1 column; and (3) an expanded section of piping in the organic discharge line downstream from a solids removal unit, which at various times consisted of a centrifuge, a supercentrifuge, or a hydroclone. On some occasions, the solids removal unit was completely by-passed. The first named sample, designated CW or 1TF, was therefore a composite sample; the second two were flowing stream samples, 1TO or TWO, and RS, respectively.[31]

Solvent samples on which radiochemical analyses were performed varied from day to day in several respects: (1) the amount of entrained solid and liquid phases; (2) the absence or presence of an emulsion; and (3) the time during which entrained solid and aqueous phases had been able to settle prior to performance of the radiochemical analyses. Some of these samples were centrifuged, some not; some were diluted with an equal volume of ethyl alcohol to homogenize the sample. After preliminary studies[36] showed that some of the activity deposited on the walls of glass sample bottles on extended contact, all subsequent organic samples were quickly transferred to polyethylene bottles.

2.2 Solvent Activities and Decontamination

Thorex Pilot Plant. Ruthenium-103-106 and zirconium-niobium-95 activities in streams entering and leaving the Thorex Pilot Plant solvent recovery system varied by a factor of $>10^5$ (Table 1). During runs HD-16 through SD-3, Ru-103-106 activities in the TBP-Amsco solvent in tank T-4 varied from 0.002 to 280 mcuries/gal, while Zr-Nb-95 activities varied from 0.0008 to 33 mcuries/gal. However, except HD-19 and SD-1, 2, and 3, all of which were short-decay runs, these activities were less than 0.68 and 2.0 mcuries/gal, respectively. For reference, the Zr-Nb-95 activity in the recovered solvent from the Hanford solvent recovery system has been stated to be 1-3 mcuries/gal.[9]

Decontamination of solvent with respect to ruthenium or zirconium-niobium by treatment with 0.1 vol of 0.1 M Na_2CO_3 in the pulsed column T-1 was relatively incomplete. With a few exceptions (Table 1) decontamination factors were less than 10, and less than 5 in seven runs out of eleven for which data are available.

As used during the Thorex Pilot Plant operations, the hydroclones apparently produced no net decontamination (Table 1). For example, while producing a decontamination factor in excess of 4 in run HD-20, in successive runs this factor was less than 1; i.e., the solvent leaving the hydroclones contained more ruthenium and zirconium-niobium than did the solvent entering the hydroclones. The data suggest either that the samples were not representative of the streams or that highly radioactive solids were carried by the organic phase from the sodium carbonate column, partially removed from this stream by deposition on the walls of the hydroclone, and subsequently released from the hydroclone.

It should be noted that the data in Table 1 summarize average decontamination factors or average recovered solvent activities. If the Pilot Plant had operated under steady-state conditions during the periods between first and last samples from each run, such averages would provide information on the effectiveness, for example, of the sodium carbonate system. However, steady-state operation of the Pilot Plant solvent recovery system was very rare (Figs. 1-3), rendering evaluation of the system as a whole or of an individual purification step nearly impossible.

Purex Pilot Plant. Solvent recovery was in an experimental stage during the ORNL development of the Purex process. Early use of sodium carbonate was with batch contactors;[6] toward the end of this development the sodium carbonate pulsed column was introduced. In most cases the carbonate wash was followed by a water wash. This, however, was found to be of little use when centrifuges were also used. Decontamination of solvent across individual process units was not measured; instead, only beta activities of used solvent and recovered solvent were determined, in terms of counts per milliliter. As shown in Table 2 (taken from reference 6) the decontamination factors of first-cycle waste solvent from ruthenium, zirconium, and niobium varied from 8 to 14; corresponding decontamination factors for the second uranium cycle waste solvent were 2.2-3.

Table 1. Ruthenium and Zirconium-Niobium Activities and Decontamination in Thorex Pilot Plant Runs[a]

| Run No.[b] | Ruthenium | | | | Zirconium-Niobium-95 | | | |
| | Activity, mcurie/gal | | Avg D. F. | | Activity, mcurie/gal | | Avg D. F. | |
	Max in T-4	Avg in Recovered Solvent	Across T-Column[c]	Across Hydroclone[d]	Max in T-4	Avg in Recovered Solvent	Across T-Column[c]	Across Hydroclone[d]
HD-16	0.07	0.0037	2.6	1.8	0.62	0.024	1.1	5.5
HD-17	0.06	0.0061			0.052	0.010		
HD-18	0.04	0.0069			0.15	0.011		
HD-19	4.7	1.25	2.9	0.92	1.3	0.54	1.4	1.1
HD-20	0.07	0.035	4.5	4.5	2.0	0.12	3.3	4.9
HD-21	0.002	0.0008	3.0	0.7	0.085	0.039	2.9	0.76
HD-23	0.16	0.060	5.2	0.25	0.37	0.054	17	0.14
HD-24	0.10	0.044	6.2	0.19	0.056	0.033	4.9	0.18
HD-25	0.02	0.0012	2.8	2.1	0.075	0.0018	18	0.96
HD-26	0.04	0.0009	8.2	1.4	0.16	0.0057	8.7	1.1
HD-27	0.68	0.28			0.11	0.064		
SD-1	55	9.9	4.3		2.6	0.46	3.7	
SD-2	280	33	4.5		4.7	1.0	2.7	
SD-3	12	0.17	41		1.5	0.0056	145	

[a] Blank spaces in this table indicate samples were not taken.

[b] All runs prior to HD-20 used one cycle of solvent extraction; runs HD-20 et seq. used two cycles of solvent extraction, according to Co-decontamination Flowsheet.[31]

[c] Average activity in CW/average in TWO.

[d] Average activity in TWO/average activity in RS.

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Table 2. <u>Average Solvent Activities and Solvent Decontamination in Purex Pilot Plant</u>[a]

Solvent recovery system: sodium carbonate, aqueous wash tanks or columns,
water wash columns, and centrifuges

	Activities								
	c min^{-1} ml^{-1}			mcurie/gal			Avg D.F.		
Run Nos.	Ru β	Zr β	Nb β	Ru β[b]	Zr β[c]	Nb β[d]	Ru β	Zr β	Nb β
First Cycle Used Solvent									
HCP-3—HCP-15[e,f]	2.7×10^4	1.2×10^4	4.1×10^3	1.8	0.53	1.3	12	8	14
HCP-16—HCP-19[g,h]	3.8×10^4	7.8×10^3	1.6×10^3	3.8	0.35	0.51	14.7	4.6	12.7
Second Uranium Cycle Used Solvent									
HCP-3—HCP-15[e,i]	7.9×10^2	25	37	0.054	0.0011	0.012	2.9	2.1	3
HCP-16—HCP-19[g,i]	7.6×10^2	42	69	0.077	0.0019	0.022	5.3	1.9	4.9

[a]For details see reference 6, from which table was taken.

[b]Converted by use of factor 40.1 d/m = 1 c/m for HCP-3 through HCP-15 and 59.2 d/m = 1 c/m for HCP-17 through HCP-19 for Ru-103-Ru-106 mixtures. See appendix.

[c]Converted by use[33] of factor 26 d/m = 1 c/m for Zr-95.

[d]Converted by use[33] of factor 185 d/m = 1 c/m for Nb-95.

[e]Fuel decayed more than 90 days.

[f]Recovery system was sodium carbonate wash column (0.1 vol aq. 0.2 $\underline{M}$ Na$_2$CO$_3$) followed by water wash column.

[g]Fuel decayed about 60 days.

[h]Same as footnote f except water wash column was replaced by centrifuge or supercentrifuge.

[i]Recovery system was sodium carbonate wash column, water wash column, and centrifuge.

GROSS DF's ACROSS SOLVENT RECOVERY SYSTEM

1.12
>11.9
>10.6
2.3
1.7
0.096
4.3
2.2
1.9
3.7
1.6
2.1
0.67
1.4
3.5
0.29
0.92
4.5
1.4
3.9
0.62
0.44
0.21
0.36
0.52
1.8
0.33
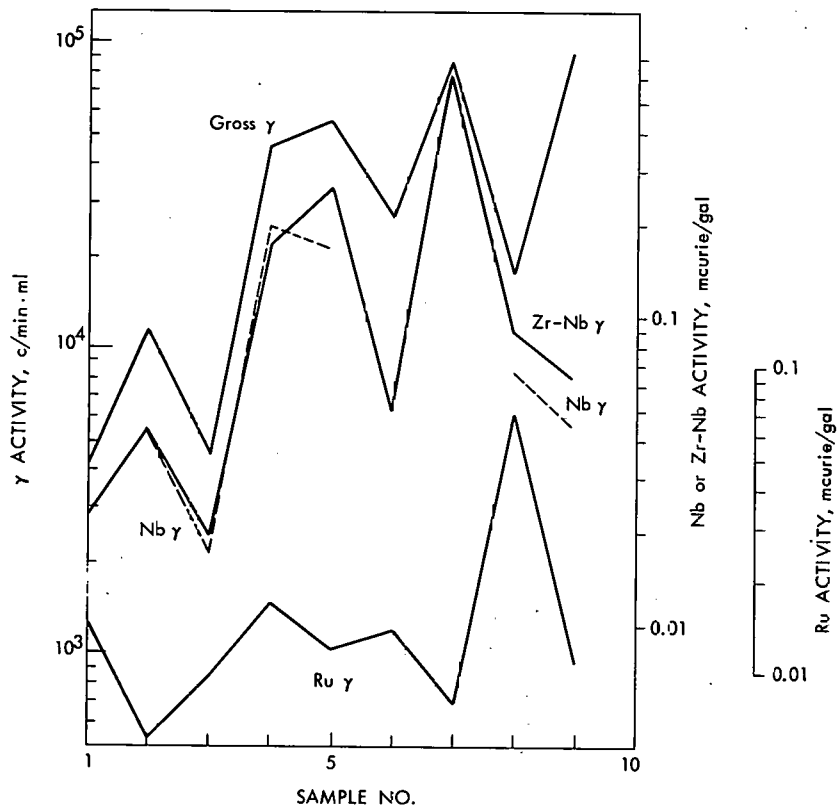
Fig. 1. Gamma activities in tank T-4 in Thorex
Pilot Plant Run HD-16. Sampling at rate of approxi-
mately once per day.
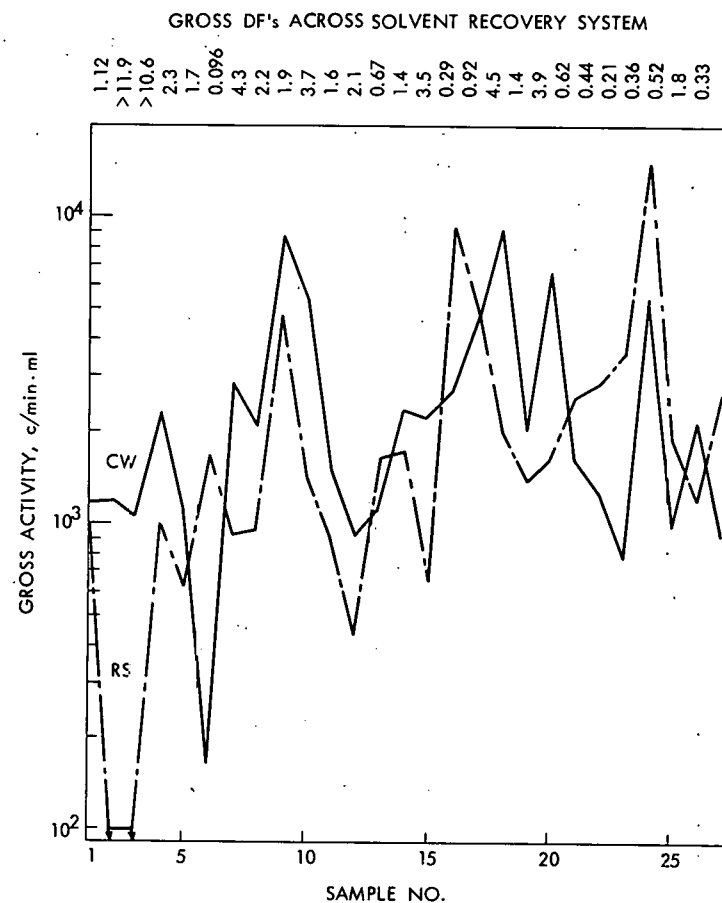
Fig. 2. Gross γ activities in waste and recovered
solvent streams in Thorex Run HD-17.

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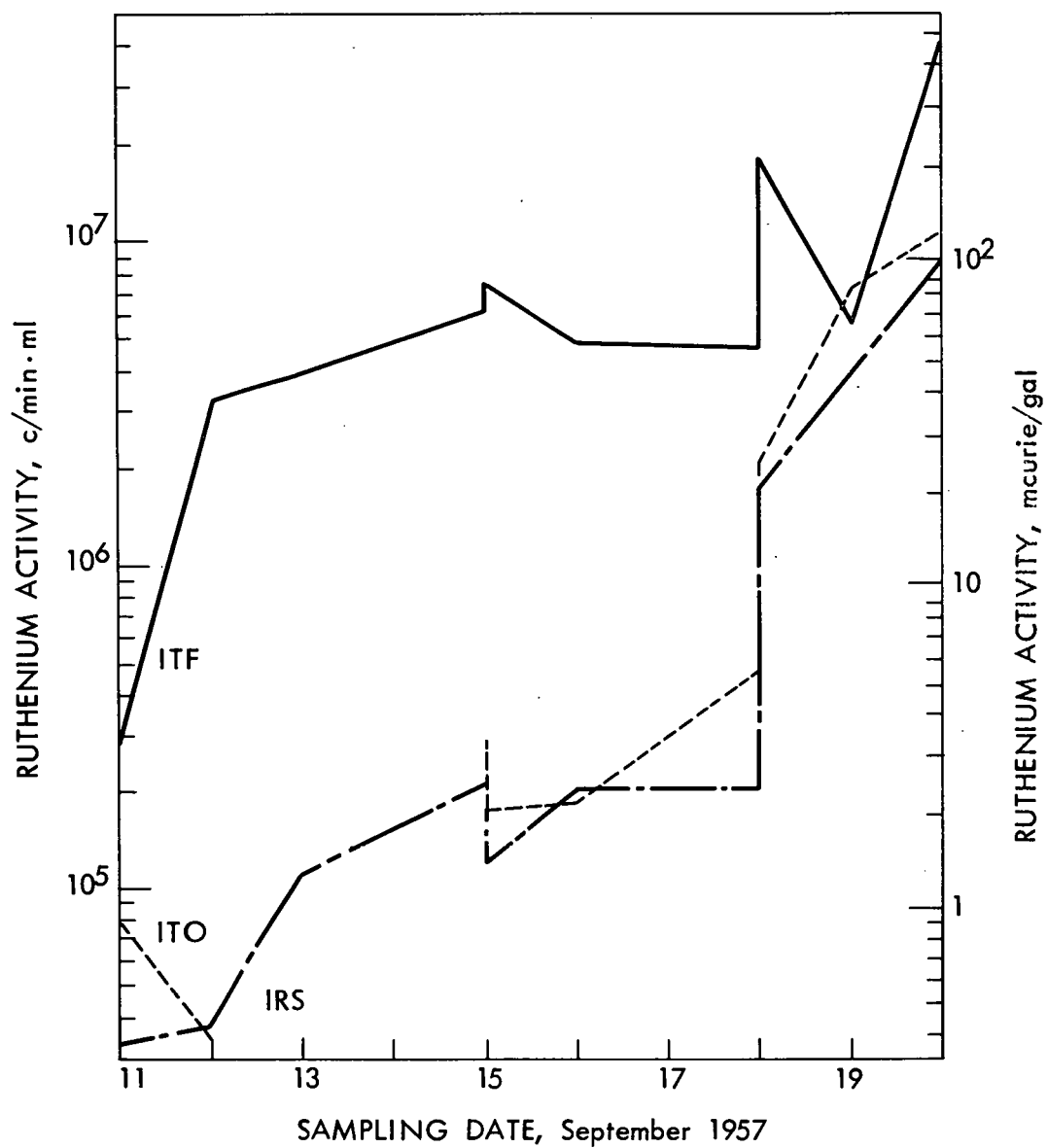
RUTHENIUM DECONTAMINATION FACTORS

3.5	97		26	26		13	0.8	4.0	across IT
			34			8.9			
2.5	0.9		1.4	0.9		1.8	1.8	1.2	across hydroclone
			1.6			1.2			

Fig. 3. Decontamination from ruthenium in solvent recovery system, Run SD-2.

Absolute activities of waste solvent were not reported in the Purex process terminal report,[6] but these may be calculated from beta counting efficiency factors that are available[25] (see appendix). Specifically, the counting efficiencies for Zr-95 and Nb-95 on the second shelf (nominal 10.18%[6]) were 3.85% and 0.54%, respectively;[33] the efficiency for ruthenium determination varied with fuel cooling time, due to the varying ratio of Ru-103/Ru-106, from 1.69 to 2.49% (see appendix). Thus, activities of Zr-95 and Nb-95 in millicuries per gallon are fairly accurate; those of ruthenium are probably uncertain by ±20% of the listed values (Table 2). In spite of the uncertainties, it is apparent that the activities of ruthenium, zirconium, and niobium were each of the order of 1 mcurie/gal in the Purex first cycle waste streams. They are in general, but not in all cases, higher than the corresponding 1CW activities observed in the long-decayed Thorex Pilot Plant runs, HD-27 and earlier (Table 1).

2.3 Laboratory Studies

Since the early findings[11] that mono- and dibutyl phosphoric acids were degradation products of tributyl phosphate, laboratory studies[19,23,34] have been mainly concerned with the use of aqueous alkaline solutions or slurries, which could reasonably be expected to neutralize these acids and convert them to aqueous-soluble species. The difference between low-level activity solvent decontamination factors[13,19] or acid removal factors,[34] which are both of the order of 20-100, and the low waste-solvent decontamination factors of approximately 10 achieved in pilot and production plants (Table 2, references 6, 9, and 22) suggests that either the neutralization philosophy is incorrect or that the process equipment does not operate very efficiently.

In considering removal of mono- and dibutyl phosphoric acids from TBP, the possible existence of these as complexes with fission products has generally been disregarded. For example, uranium irradiated to the level of 500 Mwd/metric ton contains approximately 500 g of fission products per metric ton of uranium. If the average atomic weight of a fission product is assumed to be 119 and its average cationic valency +2, then there is 2×10^{-3} equivalent of fission product per mole of uranium or 3.6×10^{-3} equivalent per liter of aqueous solution if that solution contains 1.8 $\underline{M}$ uranium, as in the Purex process. In the Purex process[15] 4.73 liters of 30% TBP in hydrocarbon diluent (1.13 $\underline{M}$ TBP) is contacted with 1 liter of aqueous feed. Therefore, if 0.01% of the TBP was decomposed to DBPA and MBPA in the ratio 2/1, there would be formed 0.000113 mole of acid degradation products, or 1.505×10^{-3} equivalent of acid per liter of organic solution, or 7.13×10^{-3} equivalent of acid per liter of aqueous solution with which this organic phase is contacted. Thus, even such a low burnup as 500 Mwd/metric ton of uranium gives enough fission products to complex a large portion, or all, of the acid degradation products from TBP. Since the more abundant uranium and plutonium also form mono- and dibutyl phosphates, recovery of waste solvent should be considered in terms of removal of fission products, uranium, thorium, and plutonium mono- or dibutyl phosphates rather than in terms of removal of the corresponding acids.

3.0 SOLVENT CONTAMINATION AND FUEL DECONTAMINATION IN THOREX PILOT PLANT

Solvent decomposition is important to the extent that it affects product losses and product contamination. To a first approximation, which has been substantiated within a factor of about 2 in a few cases,[8,28,34] the acidic solvent degradation products mono- and dibutyl phosphoric acids complex with the cationic constituents in feed solutions according to expected stoichiometry. For example, the UO_2^{++} cation appears to form the dibutyl phosphate $UO_2[(C_4H_9O)_2POO]_2$ with dibutyl phosphoric acid, $(C_4H_9O)_2POOH$. Therefore, if TBP in a solution containing 425 g of TBP per liter in Amsco 125-82 (42.5% or 1.6 $\underline{M}$) was decomposed to DBPA and MBPA, in a mole ratio of 2/1, to the extent of 0.01%, there would be formed 0.00016 mole of acids or 0.000213 equivalent of acid per liter. Since several cations, e.g., UO_2^{++}, $Th(NO_3)_2^{++}$, and $Zr(OH)_2^{++}$, would share in complexing with these acids, the exact effects of 0.01% decomposition of TBP in the solution cannot be estimated. However, if all the acids were complexed by the individual cations, the following quantities would be so complexed: thorium as the $Th(NO_3)_2^{++}$ ion, 0.025 g of thorium per liter of solvent solution; uranium, as the $U233O_2^{++}$ ion, 0.025 g of $U233$ per liter of solvent solution; zirconium, as the $Zr(OH)_2^{++}$ ion, 0.0097 g of zirconium per liter of solvent solution. If uranium was present in the ratio 1000 g per metric ton of thorium, the thorium being introduced as an aqueous phase containing 350 g of thorium per liter and extracted into 5 volumes of organic phase, its concentration would be 0.070 g of uranium per liter of solvent solution. Since decomposition of 0.01% of the TBP in a 42.5% solution of TBP in Amsco would yield as much acidic products as would be necessary to complex about 36% of the uranium from 1000-g/t material, but since uranium in the Thorex process appeared to follow the distribution pattern expected in the absence of these acidic products, it can be concluded that uranium, as the UO_2^{++} ion, did not significantly complex the acidic TBP degradation products under Thorex conditions. This situation is probably the result of other cationic mono- or dibutyl phosphates, particularly the thorium compounds, being more stable than the corresponding uranyl compounds. The choice of 0.01% decomposition in the above example is based on known rates of radiolysis and hydrolysis of TBP.[5,29] How other solvent degradation products affect fuel recovery is not known.

In the absence of obvious effects of TBP degradation products on fuel losses, the next effects of these products to consider are thorium and uranium contamination and the decontamination of solutions of these in the solvent extraction system. Solvent from the first cycle of Thorex operations was passed through the solvent recovery system and then to the second cycle. Ruthenium and zirconium-niobium activities in recovered solvent varied from 10^2 to 10^6 c min^{-1} ml^{-1} (0.0008 mcurie/gal $<$ Ru-103-106 $<$ 33 mcuries/gal; 0.00018 mcurie/gal $<$ Zr-Nb-95 $<$ 1.0 mcurie/gal). Average decontamination factors of uranium and thorium, with respect to these nuclides, across the second cycle of solvent extraction varied widely, but did not show any correlation between decontamination factor and solvent activity (Fig. 4). In particular, decontamination of uranium from ruthenium varied from 40 to 1800; from zirconium-niobium, from 75 to 2700 (Fig. 4a). Corresponding ranges for decontamination of thorium from these fission products were 10-960 and 8-760 (Fig. 4b).
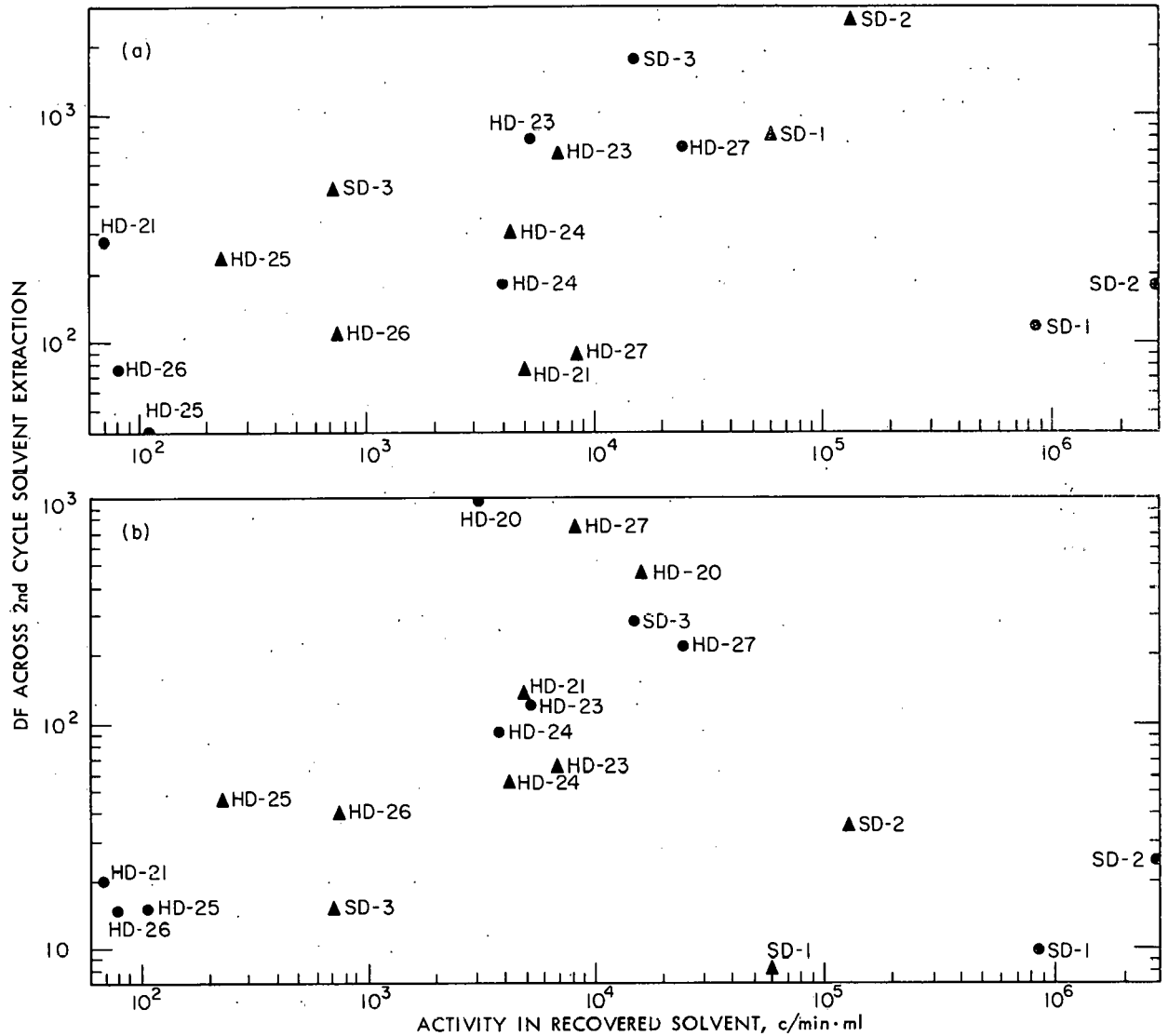
Fig. 4. Variation in (a) uranium decontamination and (b) thorium decontamination in second cycle of solvent extraction with activity in recovered solvent used as second cycle extractant. Thorex Pilot Plant. ● Ruthenium. ▲ Zirconium-niobium.
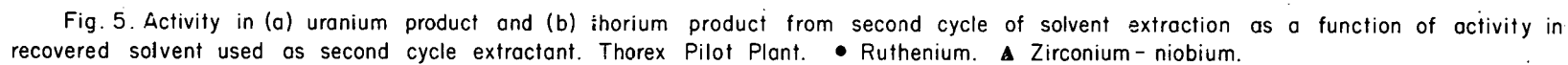
Specific activities of uranium and thorium products from the second cycle of solvent extraction are plotted against activities in solvent used in that cycle in Fig. 5. Correlation of these two parameters is extremely poor; i.e., product activity cannot be expressed as a function of solvent activity with much confidence. The activities of both uranium and thorium products from the solvent extraction step are expected to increase as feed activities increase; similarly, activity in the recovered solvent should increase as fuel feed solution activity increases. Thus, the parameters of Fig. 5 should appear to be related to each other since they are functions of the same variable.

4.0 PURITIES OF TRIBUTYL PHOSPHATE AND AMSCO 125-82

In attempting to evaluate solvent recovery methods and process difficulties caused by impurities produced during the use of TBP in Amsco 125-82, it should first be recognized that our knowledge of the purity of these two materials in the "as received" state is meager. Amsco 125-82 is purchased primarily on the basis of its physical properties and knowledge that the amount of olefinic impurity is small; TBP is purchased as a technical-grade chemical. Generally, new solvent and diluent are added to the ORNL Pilot Plant upstream from the solvent recovery equipment. Hence, water-soluble impurities in the "as received" chemicals should be removed by the aqueous sodium carbonate solution.

Kennedy and Grimley[16] have given thorough consideration to the contaminants that might be expected in commercial TBP. They report their particular sample contained the following impurities: dibutyl phosphate (dibutyl phosphoric acid), 2.07 g/100 ml; ammonia, 0.8 g/100 ml; tetrabutyl pyrophosphate, 0.15 g/100 ml; n-butyraldehyde, 0.03 g/100 ml; n-butanol, 3.4 vol %; chloride, nil; monobutyl phosphate (monobutyl phosphoric acid), nil; dibutyl hydrogen phosphite, nil. Dibutyl phosphoric acid and n-butanol were therefore present in considerably greater amounts than would be formed by dealkylation and radiolysis during extended use of TBP in radiochemical processing. Since analysis of only one sample was reported by Kennedy and Grimley, the data cannot be considered representative of commercial TBP in general. However, these analyses suggest that until the contrary is proved, impurities in commercial TBP should be suspected of being a major source of chemical difficulties in solvent extraction and solvent recovery processes.

Amsco 125-82 is a mixture of branched chain hydrocarbons. Hence, the word "impurity" as applied to this diluent does not have the usual meaning of quantity of contaminant with respect to a pure compound. Rather, impurity here refers to any component that may cause difficulty in solvent extraction. The role of diluent impurities is not well defined. For example, alkenes can be expected to add iodine, including the radioactive isotopes, to the C=C grouping, thereby binding this element in a very stable structure. Or, this same double bond structure can be oxidized to carboxylic acids which could form compounds with various elements present in feed solutions. At present, it is not possible to say what specific impurities in Amsco 125-82 should be removed prior to use of this diluent in solvent extraction.

Fig. 5. Activity in (a) uranium product and (b) thorium product from second cycle of solvent extraction as a function of activity in recovered solvent used as second cycle extractant. Thorex Pilot Plant. ● Ruthenium. ▲ Zirconium – niobium.

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5.0 DISCUSSION AND CONCLUSIONS

Treatment of solvent prior to recycling it in solvent extraction operations is necessary only because of one, or a combination, of the following reasons: untreated solvent (1) causes excess product losses, (2) prevents attainment of product specifications, and (3) in the case of radiochemical operations, presents a radiation hazard. In the Thorex and Purex Pilot Plants at ORNL, the radiation hazard applied because the recovered-solvent storage tanks were unshielded or unit-shielded in normal personnel access areas. Since the storage tanks will soon be within shielded areas, it seems desirable to determine whether waste solvent treatment was or will be necessary for process performance reasons.

Hanford first cycle, 1CW, waste solvent contains, on the average,[9] 20 to 30 mcuries of Ru + Zr + Nb γ activity per gallon; recovered 1CW solvent contains about 2 mcuries/gal. This latter level is adequately low for the solvent to be recycled to the first cycle system and can serve as a tentative reference with which to compare activities in the solvent recovery system streams at ORNL (Fig. 6). In addition, the 2EW and recovered 2EW activities, approximately 0.2 and 0.03 mcurie/gal, respectively, at Hanford afford a tentative reference for other second cycle solvent activities. A final, tentative reference point for first cycle recovered solvent is the value 4-5 mcuries/gal (Fig. 6). If recovered 1CW solvent exceeds this value, Hanford experience[9] shows that difficulty in attaining plutonium product specifications for Zr-95 will be encountered. Comparison of the average 2 mcuries (Ru + Zr + Nb)/gal in recovered 1CW with this "maximum permissible value" of 4-5 mcuries/gal implies that the Hanford recovered first cycle solvent is better than necessary by a factor of only approximately 2. Using these Hanford references, the following comparisons can be made:

1. ORNL Purex Pilot Plant 1CW and recovered 1CW stream activities were lower than the corresponding Hanford values by a factor of about 4, on the average, while ORNL and Hanford 2EW and recovered 2EW stream activities were nearly identical. Thus, the ORNL Purex Pilot Plant was a good predictor of solvent activity results to be expected in a production plant (Fig. 6). It should be noted that different diluents were used in these plants.

2. Activities in T-4 in ORNL Thorex long-decay runs (approximately equivalent processwise to the Hanford 1CW stream) were actually lower, on the average, than recovered 1CW solvent at Hanford. Although there was a wide spread in activities in treated 1CW solvent from the Thorex long-decay runs, on the average it contained only about the same activity as recovered 2EW solvent at Hanford, namely a few hundredths of a millicurie per gallon. Thus, activities in solvent recovered from the first cycle were low enough for use of this solvent in the second cycle in the Thorex long-decay runs if reference to the Hanford Purex process is valid (Fig. 6).

HANFORD
PUREX PROCESS

ORNL
PUREX PILOT PLANT
(Only Average Values)

ORNL THOREX
LONG DECAY RUNS
(Excluding HD-19)

ORNL THOREX
SHORT DECAY RUNS
(Including HD-19)

1000

Estimated ICW Level
Including Iodine

100

10^8

10^7

10

Appx. Max. Activity for Usable, Recov. ICW

ICW

Max. in T-4

10^6

ICW

Treated ICW

Av. in Treated ICW

1

Recovered ICW

Max. in T-4

10^5

10^4

2 EW

2 EW

Treated 2EW

Recovered 2EW

Av. In Treated ICW

0.1

0.01

10^3

0.001

Ru + Zr + Nb ACTIVITIES IN PROCESS SOLVENT (TBP in Diluent), mcuries/gal

APPROXIMATE COUNTING RATE DUE TO Ru + Zr + Nb, c min^{-1} ml^{-1}. ORNL Scale
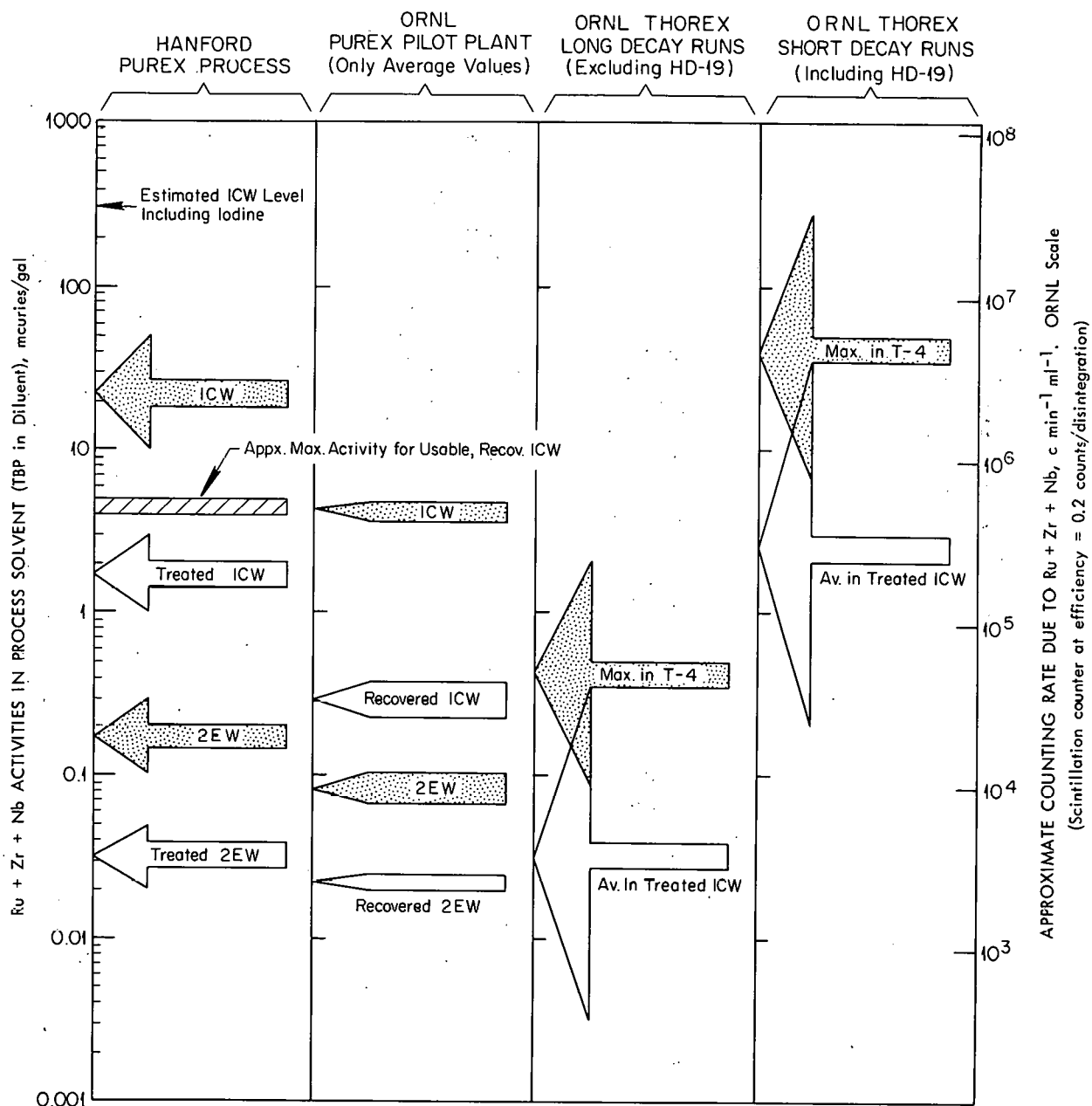(Scintillation counter at efficiency = 0.2 counts/disintegration)

Fig. 6. Ruthenium–zirconium–niobium γ or gross γ activities in process equipment. Height of arrowhead indicates the approximate variability of activity.

3. ORNL Thorex short-decay run maximum 1CW solvent activities, although representing but four runs, ranged from 0.2 to 10 times the average Hanford 1CW activities (Table 1 and Fig. 6). Corresponding Thorex recovered 1CW solvent averaged 1 to 10 times recovered Hanford 1CW solvent. Therefore, while the recovered Thorex 1CW solvent might have contained a low enough activity to be re-used in the Thorex first cycle, this activity was too high for use in the second cycle by a factor of approximately 100 if comparison with Hanford recovered 2EW activity is valid. Unless some process modification, such as changing the extraction column phase interface location, produces approximately 100-fold reduction in 1CW solvent activity, the product from any currently available first cycle solvent recovery system would not be expected to be suitable for use in the Thorex second cycle when short-decay thorium is being processed.

In the future, ORNL is scheduled to process power reactor fuels that will, in some instances, contain as much fission product power as did the Thorex SD-2 run.* Therefore, unless 1CW activities corresponding to this run can be reduced by a factor of 100, recovered 1CW solvent could not be used in a second cycle. Instead, it would be necessary to use two noninterchangeable solvent holdup and recovery systems.

Decontamination of waste solvent streams has followed a very consistent pattern at Hanford and at the ORNL Purex and Thorex Pilot Plants (Tables 1 and 2). Solvent recovery systems in all cases were based on sodium carbonate wash. The Hanford 1CW solvent recovery system also contains a unit for washing the solvent with aqueous sodium carbonate—potassium permanganate; at various times the ORNL pilot plants have used centrifuges, sand filters, and hydroclones. Yet, in all cases the long-term average solvent decontamination factor, with respect to zirconium-niobium, has been about 10, although the factor was very variable during Thorex operations (Table 1). Considering the production plant experience at Hanford, there is no present reason to expect an improvement in this value with a solvent recovery system based on carbonate or carbonate-caustic-permanganate washing unless very efficient solids-removal apparatus is also included.

Decontamination of solvent during the Thorex Pilot Plant operations was very erratic (Figs. 1-3). The reason cannot be proved conclusively, but recent studies suggest very strongly that it was due to entrainment of solids and, to a small extent, aqueous solution in the organic phase. For example, Schmitt, et al[30] tested a number of samples of 1CW solvent taken from the Bldg. 3019 pilot plant on April 13, 1959. In each case they found that the activity at the bottom of the "liquid" was about 10 times that at the top after the sample had settled a number of days. The samples used were in pint bottles that had been filled from a 2-gal polyethylene bottle of 1CW solvent. Solids were visible in that bottle. Reynolds[25,27] performed experiments on several samples of solvent to determine the origin of radioactivity. Here, again, centrifugation proved effective in reducing the activity level in the solvent, indicating the presence of solids and/or

*Consolidated Edison and Northern States Superheater fuels will be in this range.[7,35]

aqueous phases. Visual examination of solvent during Thorex operations[18,32,36] showed the presence of entrained aqueous solution, while, more recently, Rainey and Moore[24] found that the extent of removal of 1CW activity by filtration with laboratory filter paper is a function of the paper pore size, and that 99.5% of the activity can be removed by filtration through fine-grade sintered glass filters.

The role of aqueous solution entrained in the organic phase, as con-trasted with entrained solids, during solvent recovery operations has recently been clarified by Occhipinti[21] during studies of continuous washers for Purex solvent. Depending on mixing conditions, Occhipinti found that the treated solvent contained 0-0.45 vol % entrained aqueous solution. Further analyses of his data show that this entrained aqueous phase contributed a maximum of 17.6% of the total activity. Although Purex 1CW solvent was used in these experiments, the maximum activity was 1.8 mcuries/gal, approximately the same as Hanford recovered 1CW.

The adequacy of a solvent recovery system in radiochemical operations is normally expressed in terms of solvent activities and decontamination factors for gross γ, gross β, or specific γ or β activities. This is a useful measure and, at present, is the only measure in use. However, it is recognized that radioactivity may not be the best method of expressing the extent to which tributyl phosphate in a kerosene diluent is impure. It does seem probable that extensive studies would be required to obtain a measure for solvent impurity other than that based on retained radio-activity.

6.0 RECOMMENDATIONS

High radiation levels, and the associated radiolysis, of several fuels to be processed in the future at ORNL require that several factors be evaluated quantitatively. These and the recommended experiments are summarized below:

1. Determination of the decontamination achieved across the sodium carbonate wash column under steady-state conditions, including determination of the amount of activity carried by entrained solids and aqueous solution in the 1TF and 1TO streams. This will require daily sampling of solvent streams until decontamination factors are consistently repeated during a period of at least two weeks. Sampling and analytical procedures should be thoroughly re-evaluated before this test is initiated.

2. Determination of the adequacy of fission product activities as measures of solvent contamination and determination of a level at which activities of fission products in solvent are or are not deleterious to the fuel processing operation. This objective could be achieved by a detailed analysis of product activity vs. solvent activity, provided frequent sampling showed that steady-state activity existed (item 1) and provided that product activity specifications were approached or slightly exceeded.

3. Improvement in solvent repurification process. It is recommended that the primary effort on improving the solvent repurification process be performed on experimental equipment, to be located in the Bldg. 3019 Pilot Plant, which will use as feed at least 5% of the 1CW stream and which will be operated as a continuous process. Laboratory data have shown, and pilot plant data strongly imply, that repurification of solvent is primarily a solids-removal problem. Thus, solvent recovery should be studied with solids removal equipment that can, without excessive difficulty and cost, be integrated into the pilot plant.

4. Quantitative determination of impurities in a number of batches of "as received" TBP and the establishment of adequate specifications for this material and for the diluent. In addition, establishment of a use test is also recommended.

5. It is suggested that the Analytical Chemistry Division be requested to report solvent activities in terms of disintegrations per minute per milliliter, or, preferably, in terms of millicuries per gallon, rather than in terms of counts per minute per milliliter. The latter units are of limited value since they unnecessarily complicate comparison of ORNL Pilot Plant data with production plant (Hanford) data. It should be noted that whereas the ORNL scintillation counters have efficiencies[26] of approximately 20% for Ru-103, Zr-95, and Nb-95 γ activities, the Savannah River Plant efficiencies[22] are only 2.5%, another difference complicating interplant comparisons.

6. It is recommended that 2 and 0.03 mcurie (Ru + Zr + Nb)/gal be used as tentative maximum solvent activities for first and second cycle solvents. The first of these numbers is within a factor of about 2 of being equal to the value above which excessive Zr-95 occurs in the Hanford plutonium product.

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8.0 APPENDIX

Data on activities of various elements in Purex and Thorex Pilot Plants were presented in the original ORNL reports in terms of beta counts per minute per milliliter, ionization chamber millivolts produced by gamma radiation per milliliter, and scintillation gamma counts per minute per milliliter. Counting efficiencies varied between methods and between radioactive nuclides. In order to compare solvent activities at the various plants, it is necessary to convert from reported scales to a single scale. The millicurie per gallon is very convenient because the millicurie is an absolute activity and is therefore independent of counting efficiency; the gallon is a convenient unit for engineering calculations and an easily remembered reference value is the 1 mcurie/gal in the recovered 1CW solvent at Hanford (actually, as previously shown, recovered 1CW contains 2-3 mcuries/gal).

To convert disintegrations per minute per milliliter to millicuries per gallon, the former is multiplied by the factor 1.705×10^{-6} (mcurie min ml gal^{-1} d^{-1}). The remainder of this appendix contains a summary of factors for converting the c min^{-1} ml^{-1} values in the process reports to d min^{-1} ml^{-1}. The quantity γ mv/ml, which would have been of use in calculating the Ru-103/Ru-106 ratio, was not used because reported values of the quantity (β c min^{-1} ml^{-1})/(γ mv/ml) are not consistent with the known decay schemes of these nuclides, or with the calculations based on the tables of Blomeke and Todd,[2] or with the Ru-103/Ru-106 ratios reported.

8.1 Conversion Factors for Purex Pilot Plant Activities

Beta Counting Factors. Factors for converting Purex Pilot Plant activities from c min^{-1} ml^{-1} to d min^{-1} ml^{-1} were determined by Strain,[33] whose results are presented in Fig. 7. These factors are easily used for individual nuclides such as Zr-95 or Nb-95 (Table 2). In the Purex solutions ruthenium occurred as a mixture of Ru-103 and Ru-106. The factors for these are so different, i.e., 80 vs 11 d/c, that a simple average cannot be used. Instead it is necessary to calculate the fraction of Ru-103 or Ru-106 in a mixture of these by the use of additional data. The simplest method is to calculate them from the known fuel irradiation history and decay times[6] and the tables and graphs of Blomeke and Todd.[2] By this method the average value of N_6/N_3 is 1.67 for runs HCP-3 through 15 and 0.539 for runs HCP-16 through 20. The corresponding activity ratios, $\lambda_6 N_6/\lambda_3 N_3$, are 0.188 and 0.0604. Here the subscript 3 refers to Ru-103 and 6 to Ru-106.

Define

ϵ_3 = efficiency of counting Ru-103, 1 c/80 d

ϵ_6 = efficiency of counting Ru-106, 1 c/11 d

r   = counting rate, c(Ru-103 + Ru-106) min^{-1} ml^{-1}

λ_3 = decay constant of Ru-103

λ_6 = decay constant of Ru-106

Then

$$r = \epsilon_3\lambda_3N_3 + \epsilon_6\lambda_6N_6$$

Using the numerical values given above,

$$\lambda_3N_3 + \lambda_6N_6 = 40.1 \ r \text{ for runs HCP-3 through HCP-15;}$$

$$\lambda_3N_3 + \lambda_6N_6 = 59.2 \ r \text{ for runs HCP-16 through HCP-20.}$$

It should be noted that $\lambda_3N_3 + \lambda_6N_6$ is the total ruthenium (Ru-103 and Ru-106) disintegration rate in d $\min^{-1}$ ml^{-1}.

ELEMENT	β FACTOR	β's	%	WEIGHTED AVERAGE ENERGY
Ru^{103}	80	0.217 mev 0.698	99 ~1	0.223 mev
Ru^{106} (Rh^{106} daughter)	~11	3.53 3.1 2.44 2.0	68 11 12 3	3.09
Zr^{95}	26	0.371 0.84	99 1	0.375
Nb^{95}	185	0.159	100	0.159
Pr^{144} (Ce^{144} daughter)	~9	2.97	>99	2.97
Ce^{141}	~27	0.581 0.442	33 67	0.488
Y^{91}	12	1.54	100	1.54

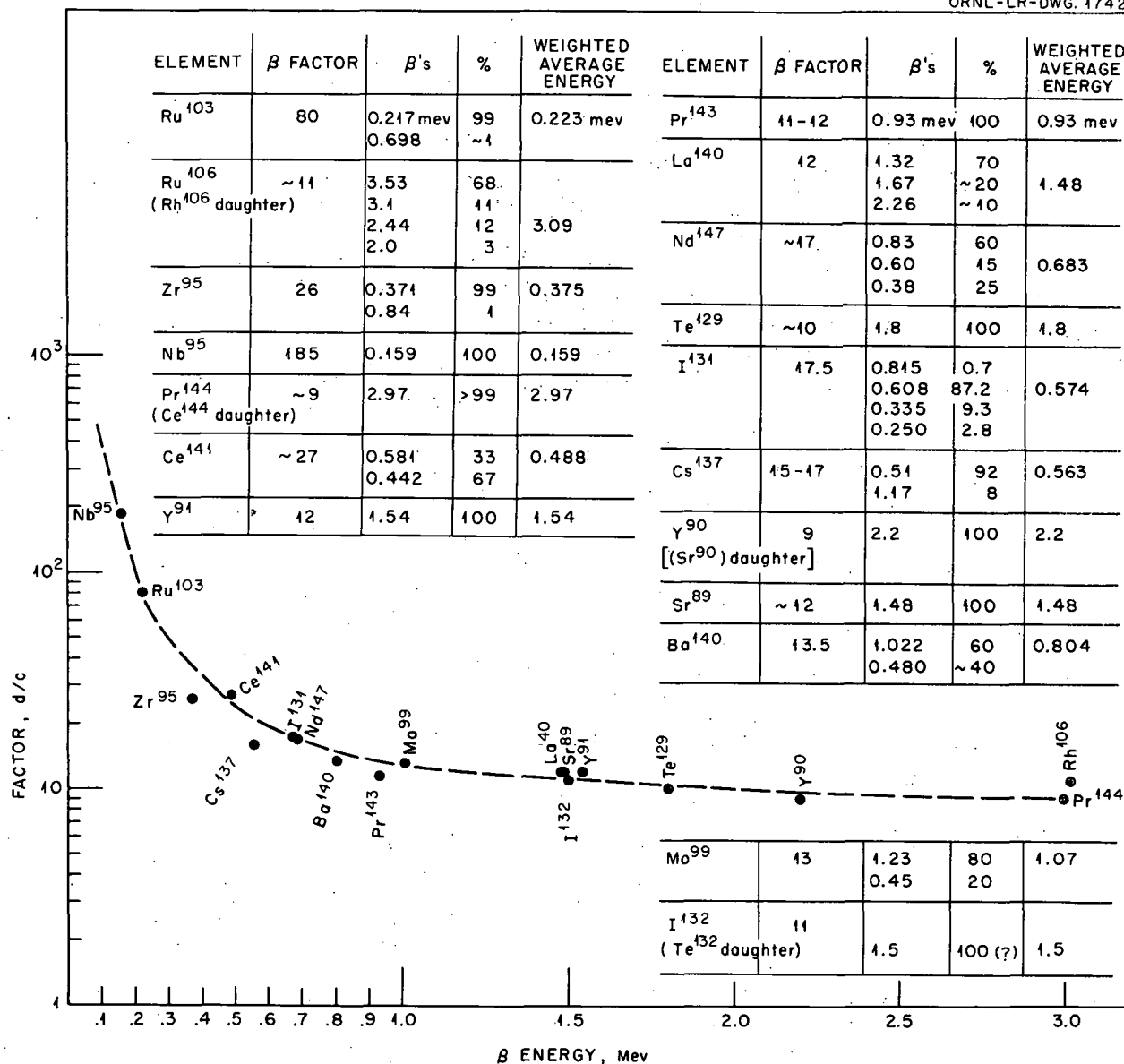| ELEMENT	β FACTOR	β's	%	WEIGHTED AVERAGE ENERGY
Pr^{143}	11–12	0.93 mev	100	0.93 mev
La^{140}	12	1.32 1.67 2.26	70 ~20 ~10	1.48
Nd^{147}	~17	0.83 0.60 0.38	60 15 25	0.683
Te^{129}	~10	1.8	100	1.8
I^{131}	17.5	0.845 0.608 0.335 0.250	0.7 87.2 9.3 2.8	0.574
Cs^{137}	15–17	0.51 1.17	92 8	0.563
Y^{90} [(Sr^{90})daughter]	9	2.2	100	2.2
Sr^{89}	~12	1.48	100	1.48
Ba^{140}	13.5	1.022 0.480	60 ~40	0.804
Mo^{99}	13	1.23 0.45	80 20	1.07
I^{132} (Te^{132} daughter)	11	1.5	100 (?)	1.5

Fig. 7. Conversion of beta counts to disintegrations. J. E. Strain, ORNL Anal. Chem. Div., 1954.

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