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Recovery of Fission Product Palladium from Acidic High Level Waste Solutions

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ABSTRACT

The recovery of palladium from a synthetic pressurized heavy water reactor high level waste (PHWR-HLW) solution has been carried out, and the best reagents to use for the actual HLW solutions are discussed. The extraction of palladium from nitric acid solutions has been carried out using Cyanex-471X (triisobutylphosphine sulfide, TIPS) as the extractant. The metal ion could be quantitatively extracted from solutions with nitric acid concentrations between 2.0 and 6.0 M. The species extracted into the organic phase was found to be $Pd(NO_3)_2 \cdot TIPS$. Nitric acid in the range of 2.0 to 5.0 M had no effect on TIPS for at least 71 hours. A systematic study of gamma irradiation on loading and stripping of palladium from loaded organic phases using several potential extractants, TIPS, alpha benzoin oxime, dioctylsulfide, and dioctylsulfoxide has been made. A flow sheet for the recovery of palladium from actual HLW solutions using TIPS is proposed.

INTRODUCTION

Due to the increase in utilization of palladium in the automotive and dental industries, in electronic and electrical devices, in the production of ultrapure hydrogen, and as an industrial catalyst, the recent demand for this metal has increased manyfold. Its global demand by the turn of the century is expected to be at least ten times greater than its production from natural resources (1). An alternative and probably the largest source for palladium is the high level waste (HLW) solutions originating from the reprocessing of irradiated fuel from nuclear reactors. A typical power reactor fuel with 25,000 MWD/t burnup will contain about 917 g palladium

(2) per ton of the fuel. Hence it is of utmost interest to design and develop an efficient and cost-effective process for the recovery of palladium from reprocessed HLW solutions originating from the PUREX process which is used almost universally for nuclear fuel reprocessing. Such solutions contain actinides (U, Np, Pu, Am, and Cm) along with a host of activation and fission products. For the recovery of palladium from such complex and concentrated solutions, the classical precipitation method using dimethylglyoxime will not be effective. The ion-exchange technique has been utilized for the recovery of palladium from aged alkaline waste solutions at Hanford (2), while many attempts have been made to recover palladium from nitric acid solutions using a variety of extractants such as tricaprylmethylammonium nitrate (3), triphenylphosphine sulfide (4), tri-*n*-octylamine (5, 6), dioctylsulfide (7), dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (8), and alpha benzoin oxime (9). Separation of palladium from platinum in the chloride medium has been attempted using Cyanex-471X (10); recently potassium iodide (11) has been suggested to extract palladium in kerosene from HLW solutions.

In the present work Cyanex-471X (triisobutylphosphine sulfide, TIPS), a commercially available reagent, has been utilized for the extraction and recovery of palladium from nitric acid solutions. Also, the effects of palladium loading, acid hydrolysis, radiation effects, and recovery of palladium from a synthetic pressurized heavy water reactor HLW solution using TIPS, alpha benzoin oxime (ABO), dioctylsulfide (DOS), and dioctylsulfoxide (DOSO) have been investigated.

EXPERIMENTAL

TIPS (American Cyanamid Co.) and ABO (GR grade from Loba Chemie) were used as extractants. DOS and DOSO were synthesized and characterized in this laboratory. The commercially available diluent Solvesso-100 was purified by contacting with 1 M HNO_3, then with 1 M NaOH, and finally (washing it) with distilled water. ^{109}Pd tracer was prepared by irradiating $(NH_4)_2PdCl_4$ in the Apsara research reactor of this center. Its radiochemical purity was checked by gamma spectrometry, and assay of the activity in aqueous and organic phases was done using a NaI(Tl) detector. All other chemicals used were of AR grade.

In all the equilibration studies, 0.5 mL each of the organic and aqueous phases were mixed for 45 minutes in a thermostated bath at 25 ± 0.1°C. The concentration of palladium in all the studies utilizing ^{109}Pd tracer was maintained at 5×10^{-5} M. After equilibration, the solutions were centrifuged, separated, and withdrawn for assay of palladium activity.

TABLE 1
Composition of the Synthetic PHWR-HLW Solution

Element	Concentration (g/L)	Element	Concentration (g/L)
		Fission Products	
Rb	0.0745	Cd	0.0159
Cs	0.5437	Sn	0.0152
Sr	0.1836	Y[a]	0.0990
Ba	0.3089	La	0.2643
Se	0.0123	Ce	0.2353
Te	0.1028	Pr[a]	0.2436
Br	0.0049	Nd	0.8624
I	0.0520	Pm[a]	0.0283
Zr	0.7714	Sm	0.1640
Mo	0.7307	Eu	0.0227
Tc[a]	0.1836	Gd	0.0165
Ru	0.4652	Pd	0.1120
Rh[a]	0.1275	Ag	0.0186
		Other Ingredients	
U	18.325	Ni	0.1000
Na	3.000	Cr	0.1000
Fe	0.500	$[H^+]$	3.11 M

[a] Y, Pr, and Pm were replaced by La; Tc by Mo; and Rh by Co.

For irradiation studies, the solutions of TIPS, ABO, DOS, and DOSO were preequilibrated with 2.0 M HNO_3 and kept for gamma irradiation to acquire a dose in the range of 0 to 50 Mrad using a ^{60}Co gamma source. The dose rate of the extractant solutions was evaluated by Fricke's dosimetry after applying corrections as given in Refs. 12 and 13.

The synthetic PHWR-HLW solution (assuming 6500 MWD/t burnup, a cooling period of 3 years, and an estimated 800 L/t of HLW produced) was prepared in HNO_3, and the final acidity was estimated by titration. The composition is given in Table 1.

RESULTS AND DISCUSSION

Variation of Distribution Ratio as a Function of Contact Time and HNO_3 Concentration

Figure 1 gives the plot of distribution ratio (*D*) of palladium from 2.0 M HNO_3 by TIPS in Solvesso-100 as a function of equilibration time. It can be seen that *D* becomes constant after 45 minutes. Hence, the aqueous

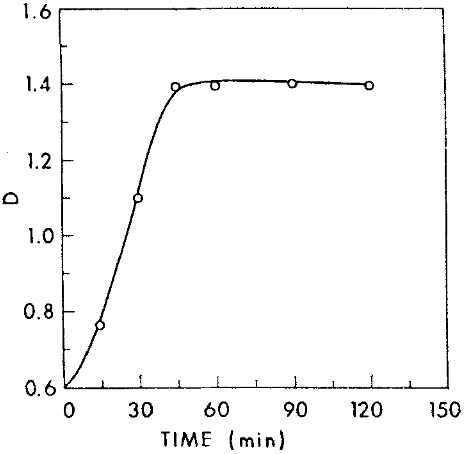

FIG. 1 Extraction behavior of Pd with TIPS from 2.0 M HNO_3 with respect to time.

and organic phases were mixed for at least 45 minutes in all equilibration studies. The effect of increasing the HNO_3 concentration on the D values of palladium is given in Table 2. It is concluded that the D values increase up to a concentration of 2.0 M of HNO_3 and then remain more or less constant up to 6.0 M.

The extraction of actinides U(VI), Pu(IV), and Am(III) from 2.0 M HNO_3 was found to be very small, with $D < 0.01$, whereas in the case of Ru(III) the D value was found to be about 0.02. Although all these metals were extracted into the organic phase, the organic phase showed activity below the detection limit after a scrub with 2.0 M HNO_3. In the case of Rh(III), the concentration was varied in the range of 3.9×10^{-4} to 4.8×10^{-3} M while keeping the Pd concentration at 5×10^{-5} M and extracting with 1×10^{-4} M TIPS, the D value of Pd remained constant and the same as those observed in the absence of Rh(III). It was therefore inferred that Rh(III) is not extracted under the experimental conditions.

During the course of extraction and recovery studies of palladium with TIPS, various nitric acid concentrations may be encountered, and it was

TABLE 2

Distribution Ratio of Pd with Respect to HNO_3 Concentration ([TIPS] = 1×10^{-4} M)

$[HNO_3]$, M	0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0
D	0.64	0.81	0.96	1.36	1.40	1.47	1.58	1.60

TABLE 3
Effect of HNO_3 Concentration and Contact Time on the Degradation of TIPS
([TIPS] = 1×10^{-4} M)

	Contact time (hours)						
$[HNO_3]$, M	0.25	8.0	24.0	30.5	47.5	54.0	71.0
	Distribution ratio						
2.0	1.60	1.44	1.65	1.45	1.40	1.55	1.71
3.0	1.38	1.45	1.60	1.61	1.55	1.60	1.60
4.0	1.51	1.41	1.55	1.45	1.51	1.56	1.70
5.0	1.65	1.45	1.45	1.35	1.61	1.45	1.46

important to study the effects of contact time and different nitric acid concentrations on TIPS and then evaluate the effects on *D* for palladium. Table 3 gives the *D* values of palladium at contact times between 0.25 and 71 hours and HNO_3 concentrations between 2.0 and 5.0 M. The *D* values do not change significantly (average value 1.55 ± 0.15), indicating a high chemical stability of TIPS even when in contact with 5.0 M HNO_3 for 71 hours.

Nature of the Species Extracted

To establish the nature of the species extracted into the organic phase, the mole ratio method was utilized. It can be inferred from Fig. 2 that the

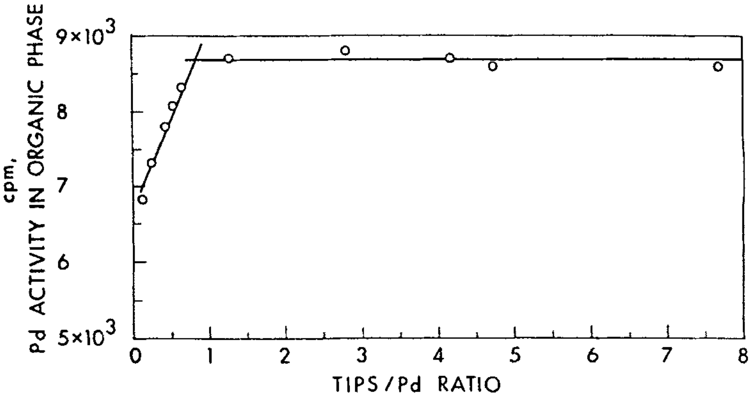

FIG. 2 Mole ratio plot of the Pd–TIPS system at 2.0 M HNO_3.

stoichiometry of the species (Pd to TIPS ratio) is 1:1. The equilibrium for this reaction can be written as

$$Pd^{2+}(a) + 2NO_3^-(a) + TIPS(o) \rightleftharpoons Pd(NO_3)_2{\cdot}TIPS(o) \qquad (1)$$

where (a) and (o) represent the aqueous and organic phases, respectively.

Effect of Gamma Irradiation on the Extractants for the Extraction of Palladium

During the course of recovery of palladium from HLW solutions, the beta and gamma doses to the extractant are very high. Therefore, the effects of gamma irradiation on TIPS were investigated. For comparison purposes, other potential extractants for palladium (ABO, DOS, and DOSO) were irradiated and the extraction of palladium were also checked at doses between 9.9 and 49.5 Mrad.

Table 4 gives the values of palladium with unwashed gamma irradiated solutions. With TIPS, the *D* value increases up to a dose of 19.8 Mrad and then remains constant up to a dose of 49.5 Mrad, the highest dose studied in the present work. It appears that some radiolytic products are formed which enhance the extraction of palladium initially, and at radiation doses of 19.8 Mrad and above the formation and destruction of those products reach steady-state conditions. With ABO, the *D* value for palladium also initially increases with increasing gamma dose but then remains constant in the dose range of 9.9 to 49.5 Mrad. With DOS there is an abrupt decrease in the *D* value of palladium from about 14 to 4 between 0 and 9.9 Mrad, then from 9.9 to 19.8 Mrad it increases to about 9 and remains constant up to a dose of 49.5 Mrad. There was practically no

TABLE 4
Distribution Ratio of Pd(II) with Different Reagents at Varying Gamma Irradiation Doses (unwashed solutions)

	Gamma dose (Mrad)					
Reagent concentration	0	9.9	19.8	29.7	39.6	49.5
	Distribution ratio					
TIPS, 1×10^{-4} M	1.38	4.79	9.13	8.98	9.17	9.11
ABO, 1×10^{-4} M	1.70	8.90	9.32	9.01	9.24	9.60
DOS, 5×10^{-4} M	13.74	4.38	8.88	9.11	9.47	9.30
DOSO, 5×10^{-2} M	16.50	17.20	18.65	17.50	17.62	18.01

effect of radiation of DOSO on the extraction of palladium over the conditions tested.

To detect the presence and the effects of any degradation products formed during the irradiation of these reagents, solutions irradiated at different doses were washed with 0.2 M sodium carbonate and reconditioned with 2.0 M HNO_3, and then the extraction of palladium was studied with each reagent. The data in Table 5 suggest that acidic degradation products are not present in irradiated samples in any of the four systems. The present interest in studies of the effect of irradiation on these reagents is mainly to assess the feasibility of extracting palladium from radioactive waste solutions, and at the present time it is not possible to give any explanation regarding the formation of new extractants (with even greater *D* values).

Loading experiments with 0.01 M TIPS, ABO, DOS, and DOSO were made with varying concentrations of palladium in the aqueous phase. In the case of TIPS and DOS (Table 6), the reagent could be loaded up to ~100% at a concentration of 1.13×10^{-2} M palladium. In the case of ABO and DOSO, the same concentration of reagent could be loaded to ~100% at a much lower concentration of palladium (8×10^{-3} M). This could be due to the formation of a 1:2 stoichiometric species in the case of ABO and DOSO (7, 9) and the formation of a 1:1 stoichiometric species in the case of TIPS and DOS.

Stripping of the Organic Phase

The stripping of palladium from the loaded TIPS phase was carried out using thiourea in the 0.01 to 0.05 M concentration range (Table 7). Quantitative backextraction was achieved even with the lowest concentra-

TABLE 5

Distribution Ratio of Pd(II) with Different Reagents at Varying Gamma Irradiation Doses (washed with 0.2 M Na_2CO_3 solution and preequilibrated with 2 M HNO_3)

	Gamma dose (Mrad)					
Reagent concentration	0	9.9	19.8	29.7	39.6	49.5
	Distribution ratio					
TIPS, 1×10^{-4} M	1.41	4.81	8.13	9.20	9.68	9.10
ABO, 1×10^{-4} M	1.68	9.30	9.19	9.40	9.60	9.60
DOS, 5×10^{-4} M	13.40	4.51	8.49	9.00	9.50	9.40
DOSO, 5×10^{-2} M	16.48	17.00	16.44	16.80	18.20	17.50

TABLE 6
Effect of Loading of Pd on TIPS, ABO, DOS, and DOSO
(reagent concentration = 1 × 10^{-2} M)

Pd in aqueous phase, M	% Loading[a]			
	TIPS	ABO	DOS	DOSO
1.132×10^{-3}	11.3	22.3	11.2	20.2
2.264×10^{-3}	22.5	43.4	22.4	41.2
4.528×10^{-3}	45.1	77.2	45.0	81.0
7.924×10^{-3}	78.2	100.0	78.4	100.0
1.132×10^{-2}	100.0		100.0	

[a] The percentage loading has been calculated by taking PD to TIPS and DOS stoichiometry as 1:1 and that with ABO and DOSO as 1:2.

tion, 0.01 M, of thiourea at an organic to aqueous ratio of 1:1. In further experiments the stripping of palladium from loaded TIPS, ABO, DOS, and DOSO phases was carried out using 0.02 M thiourea. Except for the case of ABO where the backextraction of palladium was only ~83%, quantitative stripping was achieved in all the other systems in just one contact while keeping an organic to aqueous ratio of 1:1 (Table 8). The lower percentage of stripping in the case of ABO is probably due to a different mechanism of extraction of palladium, namely complex formation instead of the solvation mechanism of TIPS, DOS, and DOSO.

Stripping experiments were also performed with all of the four loaded extractants while keeping the organic to aqueous ratios at 5:1 and 10:1 and maintaining the thiourea concentration at twice that of the palladium concentration in the organic phase. The stripping pattern was the same as that observed earlier while keeping an organic to aqueous ratio of 1:1. This fact could be used advantageously for the reduction of volume when recovering palladium from dilute solutions. The stripping of palladium extracted into an irradiated solution of TIPS (dose 49.5 Mrad) was also carried out at 1:1, 5:1, and 10:1 organic to thiourea ratios. The recovery of palladium was found to be quantitative.

TABLE 7
Stripping of Pd from the Loaded TIPS Phase with Different Concentrations of Thiourea
Organic:Aqueous Ratio 1:1 ($[Pd]_{org} = 5.66 \times 10^{-3}$ M)

Thiourea, M	0.01	0.02	0.03	0.04	0.05
% Stripped	99.7	99.8	99.8	99.5	99.5

TABLE 8
Stripping of Pd from Different Loaded Organic Phases Using 0.02 M Thiourea
Organic:Aqueous Ratio 1:1

Loaded organic phase	TIPS	ABO	DOS	DOSO
% Stripped	99.8	83.2	99.8	99.8

Experiments with Simulated PHWR-HLW Solutions

The batch extraction of palladium from the synthetic PHWR-HLW solution was carried out using the four extractants TIPS, ABO, DOS, and DOSO. The results, given in Table 9, suggest that ~99% palladium is extracted in one contact with TIPS, ABO, and DOS and the remaining palladium is recovered in a second contact. The raffinate does not contain any detectable amount of palladium. In the case of DOSO, the extraction of palladium was only about 45% in the first contact and 32 and 15% in the next two contacts (Table 9). The lower extraction of palladium with DOSO as the extractant is not surprising since it is known to extract UO_2^{2+} in such acidic conditions (14). The stripping of palladium was carried out with 0.01 M thiourea from the loaded organic phases. For TIPS, DOS, and DOSO, the recovery was almost quantitative, but in the case of ABO the recovery was low (~83%).

ICP-AES analysis of the loaded organic phase (TIPS) as well as the stripped solution using 0.01 M thiourea did not show the presence of any common metallic impurities originally present in the simulated HLW solution (Table 1), except molybdenum. Approximately 7% of the initial Mo in the synthetic waste solution was removed.

TABLE 9
Extraction of Pd from Synthetic High Level Waste Solution (reagent concentration = 1×10^{-2} M)

	No. of contacts		
Reagent	I	II	III
TIPS	99.1	~0.8	—
ABO	99.1	~0.8	—
DOS	99.1	~0.8	—
DOSO	45.6	32.0	15.5

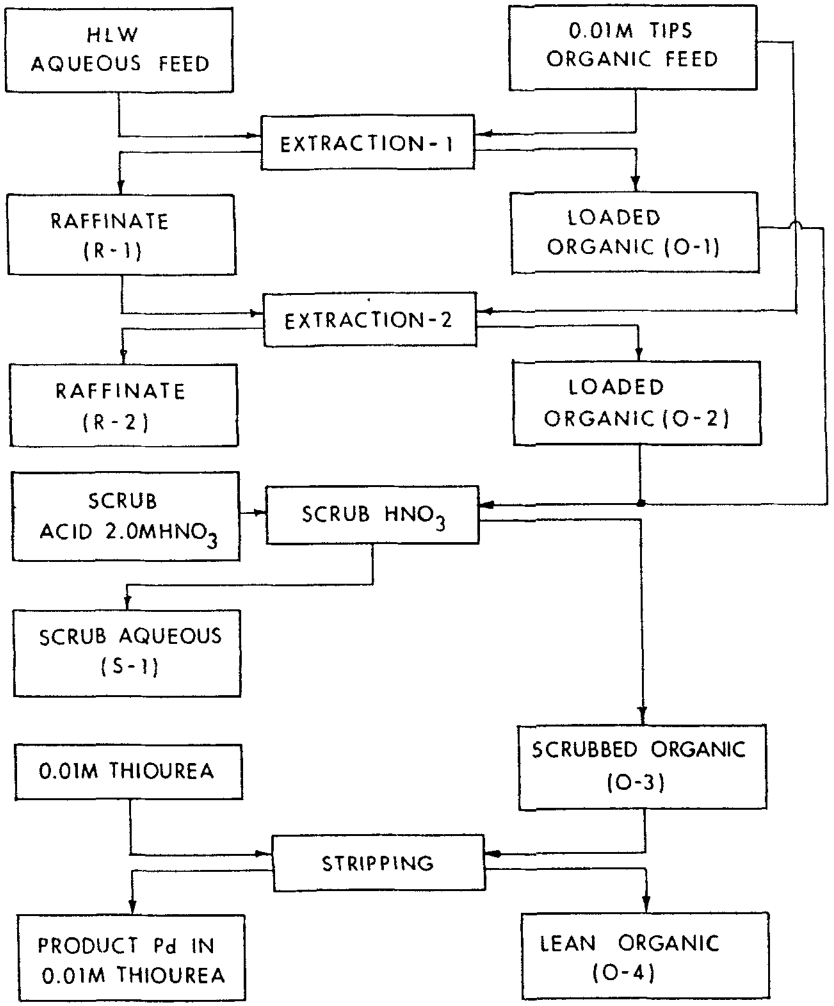

FIG. 3 Extraction and stripping scheme for the recovery of Pd from HLW solutions.

Based on the data obtained for the extraction of palladium from initial tests with HNO_3 solutions and stripping by 0.01 M thiourea, and then from tests with simulated HLW solution, a flow sheet (Fig. 3) using TIPS as the extractant is proposed for the recovery of palladium from the actual HLW solutions of PUREX origin.

CONCLUSIONS

Quantitative extraction of Pd from aqueous nitric acid solutions was achieved by using TIPS in Solvesso-100. The values for Pd remained almost constant between 2 to 6 M HNO_3. Practically no effect of HNO_3 in the range of 2 to 5 M was observed on the degradation of TIPS while keeping them under equilibration conditions for 71 hours. Gamma irradiation of TIPS and ABO showed an initial increase in the extraction of Pd, and then an almost constant value of D after further irradiation. In the case of DOS, the D value drastically decreased initially and then increased and remained constant. For DOSO, there was practically no effect of irradiation on the extraction of Pd under the doses studied (up to 49.5 Mrad). The loadings of TIPS and DOS by Pd were much higher than those of ABO and DOSO. Almost quantitative stripping of Pd was achieved by thiourea from loaded TIPS, DOS, or DOSO; with ABO it was much less effective. The extraction of Pd from the synthetic PHWR-HLW solution was quantitative in two contacts with TIPS, ABO, and DOS, while with DOSO it required three contacts to approach 90% extraction.

Although DOSO is highly radiation resistant, it cannot be used for the recovery of Pd in the presence of substantial quantities of U(VI) and Pu(IV) because these metal ions are also extracted. ABO is a good candidate but it could be loaded only with about half the quantities of Pd as TIPS and DOS. Stripping of Pd from the loaded ABO phase required extra contacts (more than one) with thiourea. For the remaining two extractants (i.e., DOS and TIPS), the only negative point with DOS is the drastic decrease in D values of Pd between 0 and 9.9 Mrad doses. Therefore, TIPS seems to be the most suitable extractant for Pd from HLW solutions of PUREX origin. Further work on the recovery of Pd from actual waste solutions will be done using TIPS as the extractant.

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