
**Defense Byproducts
Production and Utilization
Program - Noble Metal
Recovery Screening
Experiments**

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March 1986

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SUMMARY

Isotopes of the platinum metals--ruthenium, rhodium, and palladium--are produced during uranium fuel fission in nuclear reactors. The strategic values of these noble metals warrant considering their recovery from spent fuel should the spent fuel be processed after reactor discharge. A program to evaluate methods for ruthenium, rhodium, and palladium recovery from spent fuel reprocessing liquids was conducted at Pacific Northwest Laboratory (PNL).

The purpose of the work reported in this document was to evaluate several recovery processes revealed in the patent and technical literature. Beaker-scale screening tests were initiated for three potential recovery processes: precipitation during sugar denitration of nitric acid reprocessing solutions after plutonium-uranium solvent extraction, adsorption using noble metal selective chelates on active carbon, and reduction forming solid noble metal deposits on an amine-borane reductive resin. Simulated reprocessing plant solutions representing typical nitric acid liquids from defense (PUREX) or commercial fuel reprocessing facilities were formulated and used for evaluation of the three processes.

To precipitate noble metals during sugar denitration of the acidic process solution, sugar (sucrose) was added incrementally to a refluxing, simulated process solution in a stirred flask. The minimum amount of sugar used was 16 g/100 mL of solution. Precipitates formed and were filtered from the test solutions. Analyses of the filtrates using ICP^(a) showed that over 70 wt% of the palladium was removed with the precipitates. Rhodium and ruthenium recoveries were usually poor (about 3 wt% and 9 wt% maximum, respectively). However, one test using 32 g of sugar/100 mL demonstrated that higher recoveries (29 wt% of the rhodium and 44 wt% of the ruthenium precipitates) are possible. The results of these tests demonstrate that noble metals can be removed from acidic spent fuel reprocessing solutions during sugar denitration. Because these results show promise, further work is needed to optimize the process.

(a) ICP - Inductively coupled argon plasma atomic emission spectrometry.

Between 43% and 100% of the palladium in a simulated reprocessing solution was removed using carbon adsorbents containing the chelates dimethylglyoxime and phenylthiourea. The amounts were about 100 wt% from a defense-type solution and 43 wt% from a commercial type. These adsorbents removed only small percentages of rhodium and ruthenium (maximums of 11 wt% and 19 wt%, respectively) from the simulated commercial reprocessing solution.

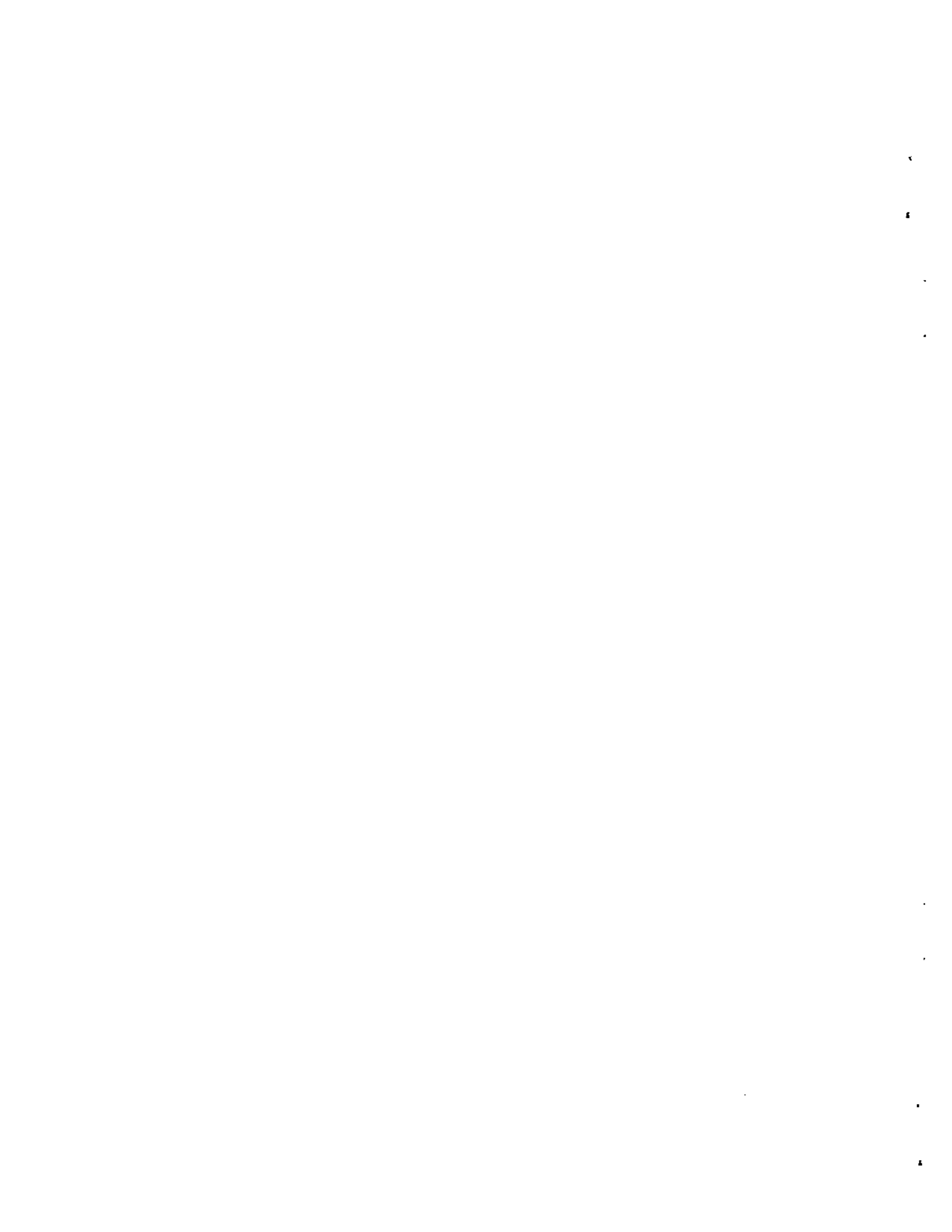
Although recovery of palladium using an amine-borane reductive resin also showed promise, rhodium and ruthenium were not recovered using this resin. Between 46% and 68% of the palladium in the simulated process solution was removed in the resin. The performance of the amine-borane resin for rhodium recovery needs more study because the resin manufacturer's literature indicates that rhodium recovery should occur. Ruthenium recovery was not expected according to this literature.

The reliability of the screening evaluations of the three processes was limited by the procedure used for analysis of solids from each test. The procedure requires steps involving solid fusion, redissolution, etc., where lost material could result in errors. Because the solid analyses were suspect, material balances could not be closed.

The screening evaluations of the three processes are preliminary. More definitive work is needed to: 1) improve solid sample preparation procedures for ICP analyses; 2) optimize operating conditions for maximum noble metal recoveries; 3) demonstrate the methods using actual radioactive waste solutions; and 4) evaluate alternative unit processes for the needed separations.

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INTRODUCTION

Isotopes of the noble metals ruthenium, rhodium, and palladium are byproducts of nuclear fuel burnup in reactors that produce plutonium at defense facilities or generate electricity at commercial power plants. Noble metals have strategic value sufficient to warrant their recovery from nuclear fuel reprocessing wastes. A lead extraction process, coupled to the high-level liquid waste (HLLW) vitrification process, has been developed and demonstrated for noble metal recovery from HLLW (Mellinger and Jensen 1982). Use of this process depends on the decision to vitrify waste and on results of further developmental studies.

Additional exploratory work is needed to 1) establish where noble metals concentrate in PUREX process streams and in what quantities, 2) determine the chemical reactions of these noble metals in PUREX process streams, and 3) evaluate alternative methods for recovery. The identification and screening evaluation of three alternative recovery processes is covered in this report.

Three potential processes have been identified to date through patent and other technical literature searches. The first process is based upon a patent^(a) (Campbell and Buxton 1981) granted to Oak Ridge National Laboratory (ORNL).^(b) In this process, palladium precipitates are produced during mixing of a denitrating sugar solution with acidic spent fuel reprocessing waste solution heated to reflux temperature. The second process is based on a patent^(a) (Moore 1974) granted to Pacific Northwest Laboratory (PNL).^(c) In this process, liquid acidic spent fuel reprocessing solutions are contacted in sequence with columns of activated carbon that have adsorbed different chelating agents specific for the metal to be recovered. The third process uses a highly porous amine-borane reductive resin placed in columns to selectively remove noble metals from pregnant liquids.

(a) Patent assigned to the U.S. Department of Energy (DOE).

(b) Operated for DOE by Martin Marietta Company.

(c) Operated for DOE by Battelle Memorial Institute.

PUREX flowsheets (Allen, Jacobs, and Reberger 1983) were examined to select the liquid waste streams that appear to offer the best opportunity for recovery of fission product noble metals. The candidates selected were 1WW (concentrated first-cycle solvent extraction acid waste), ZAW (zirflex acid waste) formed by sugar denitration of 1WW, and ZAW following neutralization. The choice of a specific process stream would depend on the specific recovery process used. One simulated process solution formulation based on the 1WW stream was selected as representative of PUREX operations; this formulation was doped with noble metal compounds and nitric acid to meet specific test needs for evaluating the three processes. Another formulation was devised to represent typical commercial spent fuel reprocessing waste.

The purpose of this report is to present results from beaker-scale screening tests performed to provide an initial evaluation of the three processes. The remainder of the report is divided into five sections: 1) conclusions and recommendations, 2) simulated acid waste solution formulations, 3) sugar denitration process evaluation, 4) chelate-impregnated carbon adsorbent process evaluation, and 5) amine-borane reductive resin process evaluation.

CONCLUSIONS AND RECOMMENDATIONS

This screening study was conducted to establish whether a few selected methods and materials could extract noble metals from simulated nuclear fuel recovery process solutions in the laboratory. No optimization work was done. Further work with nonradioactive simulated process solutions using these materials, chemistries, and possible unit process alternatives is needed to develop operating criteria to maximize noble metal recoveries. Examples of alternative unit processes that could be evaluated are fixed carbon beds (or ion-exchange resin beds) and counter-current, pulse flow of adsorbents and waste solutions in columns. This work would initially continue to use beaker-scale glassware and then, when sufficient data are developed, move on to using bench-scale or pilot-scale equipment.

All solutions used in these screening experiments were simulated spent fuel reprocessing solutions. When cold pilot-scale process evaluations using simulated process solutions including wastes are completed, proof-of-principle tests should be performed using PUREX IWW or other actual waste materials.

The following major conclusions and recommendations are based on the beaker-scale screening tests and analyses:

- Palladium can be recovered by sugar denitration of spent fuel reprocessing solutions if sufficient quantities of sugar are used. Palladium recoveries above 70 wt% were obtained from 3 N and 9 N HNO₃ simulated PUREX and commercial spent fuel reprocessing waste solutions using various amounts of sugar. In four tests, maximums of only 3 wt% of the rhodium and 9 wt% of the ruthenium were recovered; however, in one test using 3 N HNO₃ simulated commercial reprocessing solution, about 29 wt% of the rhodium and 44 wt% of the ruthenium were precipitated. This result was achieved by doubling the amount of sugar used from about 16 to 32 g/100 mL of solution over that of other tests using 3 N nitric acid solutions. These results show that all three of the platinum group metals could be recovered from acidic spent fuel reprocessing solutions during sugar denitration. Issues to be resolved before scale-up of the process to bench- or pilot-scale are optimal sugar usage, test result validation and reliable

material balances, and determination of optimal operating parameters to maximize noble metal recoveries.

- Palladium was removed from the simulated waste solutions by activated carbons containing dimethylglyoxime (DMG) and phenylthiourea (PTU). As the ratio of chelate-impregnated carbon adsorbent-to-waste solution was increased, palladium recovery was enhanced. Analyses of test filtrates show that 100 wt% of the palladium in simulated PUREX waste solution and about 43 wt% of the palladium in simulated commercial waste solution were recovered when the maximum of 2.5 g of carbon adsorbent/per 100 mL of waste solution was used. The commercial solution contains about 200 times the noble metal content than the simulated PUREX waste. Although a much larger amount of noble metals was adsorbed from the commercial waste than from PUREX waste, the percent recovery was less because the adsorbent may have reached its loading capacity. Only small percentages of rhodium and ruthenium (11 wt% and 19 wt%, respectively) were removed from the simulated commercial waste solution by carbon adsorbents at their maximum level of use (2.5 g/100 mL of waste solution).
- For screening purposes, the batch methods were convenient and useful to establish minimum recovery, equilibrium, and other factors but should not be considered as a complete test of the unit process. Absorption columns offer a lower cost processing alternative and higher loadings and, thus, need to be evaluated before a specific processing method is selected. Evaluation of specific chelates other than DMG and PTU may also be necessary to maximize recovery if rhodium and ruthenium are not removed.
- Recoveries of palladium by an amine-borane reductive resin from simulated PUREX waste solutions were satisfactory for the screening tests, but those of rhodium and ruthenium were not. Based on resin analyses, the palladium recovery from simulated PUREX waste solution was 68 wt% at the highest resin usage (1.5 g/100 mL of test solution), whereas recoveries of rhodium and ruthenium were negligible throughout the resin usage range. Poor ruthenium recovery was not unexpected; more work is needed to identify reasons for the lack of reactivity by rhodium. Palladium recovery increased progressively with higher reductive resin-to-waste solution

ratios. An increase in the contact time between the resin and the waste solution reduced palladium recovery. In this process, palladium was quickly reduced by the amine-borane resin. As the amine-borane was removed from the reaction, the reducing environment could not be maintained and palladium was oxidized off the resin. Increasing the concentration of noble metals in the test waste solution did not significantly affect the percentage of noble metal recovery. Further work should be conducted to evaluate the resins. Such work should include studies of the effects of the reductive resin upon waste solutions having higher noble metal content and the use of resin beds in adsorption columns.

- A factor affecting the reliability of test results for the three processes is the precision of analytical methods on noble metal content of the solid residues. Uncertainties arising from preparation of the solid material for instrumental analyses may have led to difficulties in closing material balances and making good comparisons or interpretations. The causes of the analytical uncertainties should be resolved for future process evaluation, both for analyzing actual PUREX process waste streams and for evaluating noble metal recovery processes.

SIMULATED ACID WASTE SOLUTION FORMULATIONS

Reference nonradioactive (cold) formulations for two simulated aqueous nitric acid waste solutions were devised: the first to simulate PUREX 1WW; the second, a typical commercial HLLW.^(a) The reference formulations are given in Table 1. The key chemical compounds used for the formulations were primarily nitrates. Preparation of the simulated solutions was difficult; some compounds only partially dissolved, or precipitation occurred following dissolution when the simulated waste solution cooled to room temperature. A similar precipitation of solids may occur with solutions from actual spent fuel reprocessing operations.

Slight variations were made from the target reference formulations during makeup of test solutions for ease of laboratory measurement and preparation of the complex mixtures. Identifying code numbers are presented in the tables for each test along with the noble metal content for a test solution. Noble metal compounds were added to each aliquot of simulated waste solution to ensure that the appropriate noble metal content was used and to avoid potential precipitation losses in a stock solution. The nitric acid content was adjusted when necessary to give a 3 N or 9 N solution, which approximate typical acid normalities for acid waste solutions described in the literature (Moore 1974; Mendel et al. 1977; Campbell and Buxton 1981) or that required for optimal noble metal recovery by sugar denitration (Campbell and Buxton 1981).

(a) Formulations based on compositions predicted for Hanford-site PUREX operations (A. C. Coroneos, Rockwell International, letter to distribution, "Composition of CAW to B-Plant," September 30, 1981; J. L. Swanson, Pacific Northwest Laboratory, letter to J. E. Minor, "Sulfate and Iron in CAW," January 6, 1982) and commercial operations (Mellinger and Jensen 1982; Mendel et al. 1977).

TABLE 1. Reference Formulations for Simulated Acid Waste Solutions^(a)

PUREX 1WW		Commercial	
Element or Ion	Concentration, g/L	Element or Ion	Concentration, g/L
H ⁺	1.12	PO ₄ ⁻²	2.4
NO ₃ ⁻	215	Cr	0.62
F ⁻	3.43	Fe	2.79
Na ⁺	2.24	Ni	0.29
Al ⁺³	22.5	Rb	0.85
PO ₄ ⁻²	0.022	Sr	2.36
SO ₄ ⁻²	16.0	Zr	9.67
Cr	0.80	Mo	11.22
Mn	0.092	Ru	5.96
Fe ⁺³	5.67	Rh	1.03
Ni	0.47	Pd	3.40
Rb	0.022	Ag	0.22
Sr	0.061	Cd	0.22
Zr	0.29	Te	1.54
Mo	0.16	Cs	7.18
Ru	0.089	Ba	3.71
Rh	0.024	Ce	14
Pd	0.017	Nd	14
Ag	0.0009		
Cd	0.0011		
Sn	0.0013		
Te	0.018		
Cs	0.13		
Ba	0.068		
Ce	0.25		
Nd	0.25		

(a) Formulations based on published information in references given on p. 7.

SUGAR DENITRATION PROCESS EVALUATION

A palladium compound can be precipitated from a strong nitric acid spent fuel reprocessing waste by adding sugar to partially denitrate the waste (Campbell and Buxton 1981; ORNL patent). A large amount of sugar is required to ensure that the precipitation occurs along with the denitration. The ORNL patent gives the empirical formula for the compound as $\text{Pd}_{1.1}\text{C}_{2.1}\text{H}_{4.1}\text{N}_2\text{O}$. However, the mechanism of reaction or the intermediate chemical forms of the palladium, rhodium, and ruthenium are unknown.

The sugar denitration process used as a basis for the ORNL work was developed by Bray and Martin (1962). In this latter process, sugar (sucrose or other sugars) added to a nitric acid spent fuel reprocessing waste solution decomposes the acid, originally at about 5 to 10 M, to give a residual free acid concentration of about 0.5 M. The reaction proceeds at 85 to 105°C; nitrogen and carbon oxide gases evolve to give a nearly sugar-free partially denitrated solution. This process is incorporated in the flowsheet of the Hanford-site PUREX plant to denitrate the 1WW stream.

As a part of the PNL program, sugar (sucrose) denitration tests similar to those described in the ORNL patent were conducted, using waste solutions simulating those predicted for Hanford-site PUREX operations^(a) and commercial operations (Mellinger and Jensen 1982; Mendell et al. 1977). The key variables in the tests were the two reference waste solutions, nitric acid normality (adjusted before testing to 3 N or 9 N), and the amount of sugar added.

About 100 to 115 mL of simulated waste solution was added to a reaction flask and heated while stirring to a refluxing temperature near 100°C. A 50 wt% aqueous solution of sugar (sucrose) was added incrementally until 20 mL was used; the mixture was then refluxed for 4 h and allowed to cool overnight. The following day, the mixture was filtered; and the precipitate and a sample of filtrate were retained for analysis. Sugar was added to the remainder of the filtrate in the reaction flask and the mixture was again refluxed for 4 h, cooled, and filtered. In some cases, the process was repeated a third time in

(a) References given on p. 7.

an effort to maximize the sugar-induced palladium precipitation. (This procedure follows the patent test program.) The precipitates and supernatants were submitted for ICP^(a) analysis (Lautensleger and Hara 1982). Only selected samples were analyzed because of funding limitations.

Table 2 gives test and available analytical data. Problems in preparing representative liquid samples from the precipitates for ICP analyses led to uncertainties in the analytical results; thus, closing material balances were not possible. This was also the case with the chelate-impregnated carbon adsorbents and amine-borane resins discussed in following sections. Although material balances were not possible, the following inferences can be made from the data available.

Based on filtrate and precipitate analyses, over 70 wt% of the palladium was removed with the precipitate from the simulated PUREX waste solution of both 3 N or 9 N HNO₃ by sugar denitration. Little rhodium (about 1 wt%) was precipitated; only 2 to 7 wt% of the ruthenium was precipitated. Both rhodium and ruthenium were identified in the precipitate.

As shown in Table 2, palladium was also effectively removed from simulated commercial spent fuel reprocessing solutions when a sufficient amount of sugar was used. About 83 wt% of the palladium was precipitated from 3 N HNO₃ commercial waste solution by the addition of 32 g of sugar/100 mL of solution; only about 22 wt% was removed by 16 g/100 mL solution. These recoveries were determined by the differences between the amount of palladium in the original test solution and that in the filtrate following reaction. The precipitate analyses support the magnitudes of the palladium recoveries. Nearly complete removal of palladium was achieved by using 62 g of sugar/100 mL of solution with the 9 N HNO₃ commercial waste solution.

Generally, rhodium precipitation in the sugar denitration was poor (less than 4 wt%) except when the amount of sugar added to a 3 N HNO₃ test solution was doubled from 16 to 32 g (see Table 2). Based on the precipitate analyses, rhodium precipitation increased to about 29 wt% in the latter test. The quantity of rhodium precipitation was affected by analytical uncertainties but

(a) ICP - Inductively coupled argon plasma atomic emission spectrometry.

TABLE 2. Noble Metal Recovery from Simulated Spent Fuel Reprocessing Wastes by Sugar Denitration

	Simulated Waste Type and Feedstock Code Number									
	PUREX		Commercial		PUREX		Commercial		Commercial	
	Stock 2	Aliquot 1	Stock 1	Aliquot 1	Stock 2	Aliquot 1	Stock 1	Aliquot 1	Stock 1	Aliquot 1
Feedstock noble metals, mg ^(a)										
Pd		1.911		428.3		1.911		428.3		428.3
Rh		2.587		103.5		2.587		103.5		103.5
Ru		10.0		600.0		10.0		600.0		600.0
Feedstock acid level										
		3N HNO ₃		3N HNO ₃		9N HNO ₃		9N HNO ₃		3N HNO ₃
Sugar, 1st addition, g										
		12.3		12.3		12.3		12.3		12.3
Sugar, 2nd addition, g										
		4.0		4.0		4.0		40		20.0
Sugar, 3rd addition, g										
						35.0		10.0		
Total, g										
		16.3		16.3		51.3		62.3		32.3
Noble metal distribution ^(b)										
	mg	wt% of feed	mg	wt% of feed	mg	wt% of feed	mg	wt% of feed	mg	wt% of feed
Pd, in precipitate										
1st	--	--	37.7	8.8	1.5	78	51.5	12.0	72	16.8
2nd	--	--	29.8	7.0	(d)	--	260.0	60.7	450	105
Total recovered	1.4	73	67.5	15.8	1.5(e)	78	311.5	72.7	522	122
Pd, in filtrate										
1st	(c)	--	389.5	90.9	(c)	--	379.9	88.7	363.6	84.9
2nd	(c)	nil	336.1	78.5	(c)	--	(c)	nil	75.0	17.5
3rd					(c)	nil	(c)	nil		
Rh, in precipitate										
1st	--	--	0.23	0.2	0.03	1.0	0.50	0.5	<0.3	<0.3
2nd	--	--	0.4	0.4	(d)	--	3.0	2.9	30.0	29.0
Total recovered	0.03	1.0	0.63	0.6	0.03	1.0	3.5	3.4	30.3	29.3
Rh, in filtrate										
1st	1.98	104	104.9	101	2.40	93	109.2	106	90.9	87.8
2nd	1.87	98	106.1	103	2.12	82	100.9	97	<12.5	<12
3rd					2.64	100	86.0	83.1		
Ru, in precipitate										
1st	--	--	22.3	3.7	0.16	1.6	12.0	2.0	22.0	3.7
2nd	--	--	29.0	4.9	(d)	--	13.0	2.2	240	40.0
Total recovered	0.65	6.5	51.3	8.6	0.16	1.6	25.0	4.2	262	43.7
Ru, in filtrate										
1st	6.20	62.0	554.3	92.4	7.19	71.9	617.0		527	87.8
2nd	6.13	61.3	539.5	89.9	6.89	68.9	553.7	92.3	375	62.5
3rd					7.56	75.6	565.7	94.3		

(a) Weights determined from analytical balance and volumetric transfer measurements. The number of decimal places shown are for future data tracking and do not indicate accuracy of measurements.

(b) Weights determined from ICP analyses.

(c) Analysis made; element content below detection level, about 0.05 µg/mL for each noble metal.

(d) No analysis made on sample.

(e) No analyses made on third precipitate resulting from third sugar addition.

is supported directionally by the low amount of rhodium (less than 12 wt%) found in the filtrate.

The pattern for ruthenium precipitation was somewhat similar to that for rhodium. Doubling the amount of added sugar to a 3 N HNO₃ simulated commercial waste solution increased the precipitation from 8.6 to 43.7 wt%. The amounts of ruthenium in the filtrates were, respectively, 89.9 wt% and 62.5 wt% of that in the feedstock.

The test results for sugar denitration show that palladium can be recovered from spent fuel reprocessing wastes if sufficient quantities of sugar are used. Campbell and Buxton (1981) identified this condition for palladium recovery in their patent; the addition of excess sugar is necessary because almost all of it reacts with nitric acid, leaving only a fraction to form the insoluble compound with palladium.

Several issues will need to be resolved before scale-up of the process. Further studies are needed to validate the test results on simulated and actual process solutions and to establish optimal operating parameters, such as the amount of sugar, rate of addition, and reflux temperature for process optimization. The inability to close material balances is believed to be due primarily to difficulty in redissolving precipitate samples from the tests obtained for analysis, not to inaccuracies in analyses of liquid feedstocks or filtrates. Analyses of solutions similar to the feedstock and filtrates were proved to be accurate by Lautensleger and Hara (1982) during development of the ICP method. In this earlier development, solutions prepared from a noble-metal-spiked calcine representative of commercial reprocessing waste were analyzed. The analytical accuracy for liquids was further demonstrated to be good in this previous study; comparisons of feedstock makeups and ICP analyses are given in Appendix A. Analyses of filtrate samples should also be accurate.

CHELATE-IMPREGNATED CARBON ADSORBENT PROCESS EVALUATION

Moore (1974) describes a process for recovering noble metals from fuel reprocessing waste solutions in which a solution is passed through an adsorption column containing a series of three chelate-impregnated carbon adsorbent beds that selectively remove specific noble metals. Each chelate-impregnated carbon adsorbent is prepared by mixing activated carbon with an ethyl alcohol solution containing a chelate at 20 to 25 wt% concentration and then evaporating the alcohol to leave the chelate adsorbed on the carbon. The chelates used (in Moore's work) were DMG for palladium recovery, diacetyldithiol (DAD) for technetium, and PTU for rhodium and ruthenium. All of these chelates form stable complex coordination compounds with platinum group metal ions and, thus, are collected in the carbon. For example, the DMG complex $\text{Pd}(\text{DGMH})_2$ is capable of forming chains of Pd atoms (Cotton and Wilkinson 1966). For details on the coordination chemistry of these materials, the reader is referred to standard texts on the subject. Following a serial contact with the waste solution, the carbon adsorbents are washed and then calcined in a closed system. The noble metals are leached from the resulting ash for recovery and eventual purification for reuse.

In screening work using a serial batch contact method, only DMG and PTU were evaluated for recovery of noble metals; no radioactive metals (e.g., technetium) were used. Carbon adsorbents were prepared as described in the PNL patent; a 14 x 60 mesh^(a) (Moore 1974) carbon was used. For testing, quantities of chelate-impregnated carbon adsorbents (0.5 to 2.5 g) were placed into Erlenmeyer flasks along with 100 mL of simulated waste solution. The materials were mixed for 1 h at room temperature and filtered. Filtrates from each DMG carbon adsorbent contact were used as feedstock for the second contact using the PTU carbon adsorbent. The filtrates and residual carbon adsorbents were submitted for ICP analyses.

Not all the ICP analyses of the filtrates and residual carbon adsorbents were completed. As was the case with sugar denitration precipitates, the

(a) Tyler mesh sizes given by the activated carbon manufacturer; equivalent sieve openings are 1.00 mm and 0.250 mm.

analyses of the solid carbon adsorbents that were made are uncertain. Nevertheless, in the absence of adsorbent analytical data, feedstock and filtrate analyses can be used to determine the removal of noble metals from solution by the carbon adsorbent. The difference in noble metal content between that of a feedstock and that of a filtrate is the amount collected in the carbon adsorbent. Use of this technique appears to be valid because the accuracy of solution analyses is good (Appendix A). Since the noble metals disappeared from solution, they had to be in the solids.

Filtrate analyses, shown in Table 3, indicate that, with the serial adsorbent contact, palladium was increasingly removed from both test waste solutions by using increasingly larger carbon adsorbents-to-waste solution ratios. Figures 1 and 2 illustrate this trend for PUREX and commercial wastes. At the lowest carbon adsorbent ratio of 0.5 g/100 mL of test solution, palladium appears to have been only slightly removed from the simulated commercial waste solution; palladium remaining in the filtrate was 97.6 wt% of that in the feedstock. However, using a ratio of 2.5 g/100 mL decreased the palladium content of the filtrate to 56.9 wt% (a 43 wt% removal of palladium from the feedstock by the carbon adsorbent).

When the simulated PUREX waste solution was used for adsorbent testing, palladium was found in only one filtrate, that obtained from the first adsorbent (OMG) contact using a ratio of 0.5 g/100 mL of feedstock. None was found in the filtrate from contacting the second adsorbent (PTU) or in any of the filtrates when higher adsorbent ratios were used. The amount of palladium in this feedstock is small (1.9 g/100 mL) compared with that in the simulated commercial waste (428 g/100 mL). Palladium may have been removed below the limit of analytical detectability.

Recovery of rhodium from either solution by carbon adsorbents was small; ruthenium recovery appears to have been a slightly larger percentage. These poor recoveries are most apparent from the results of tests using simulated commercial waste where maximum recoveries of 11 wt% for rhodium and 19 wt% for ruthenium were obtained when 2.5 g of adsorbent/100 mL of waste solution was used. Analytical results are given in Appendix B (Tables B.1 and B.2) for simulated PUREX and commercial wastes.

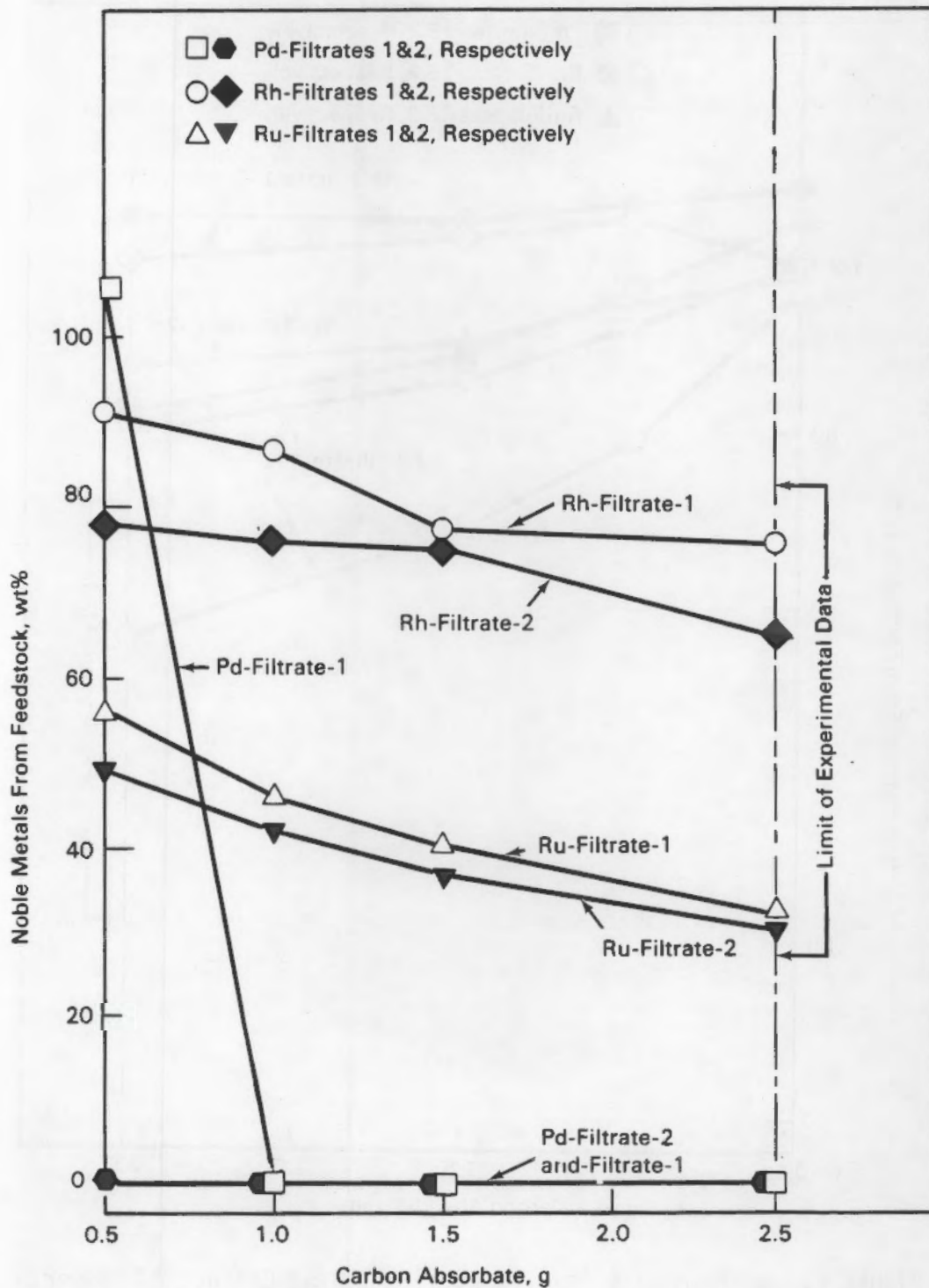


FIGURE 1. Noble Metals in Filtrates Following Contact of PUREX Simulated Waste by Chelate-Impregnated Activated Carbons

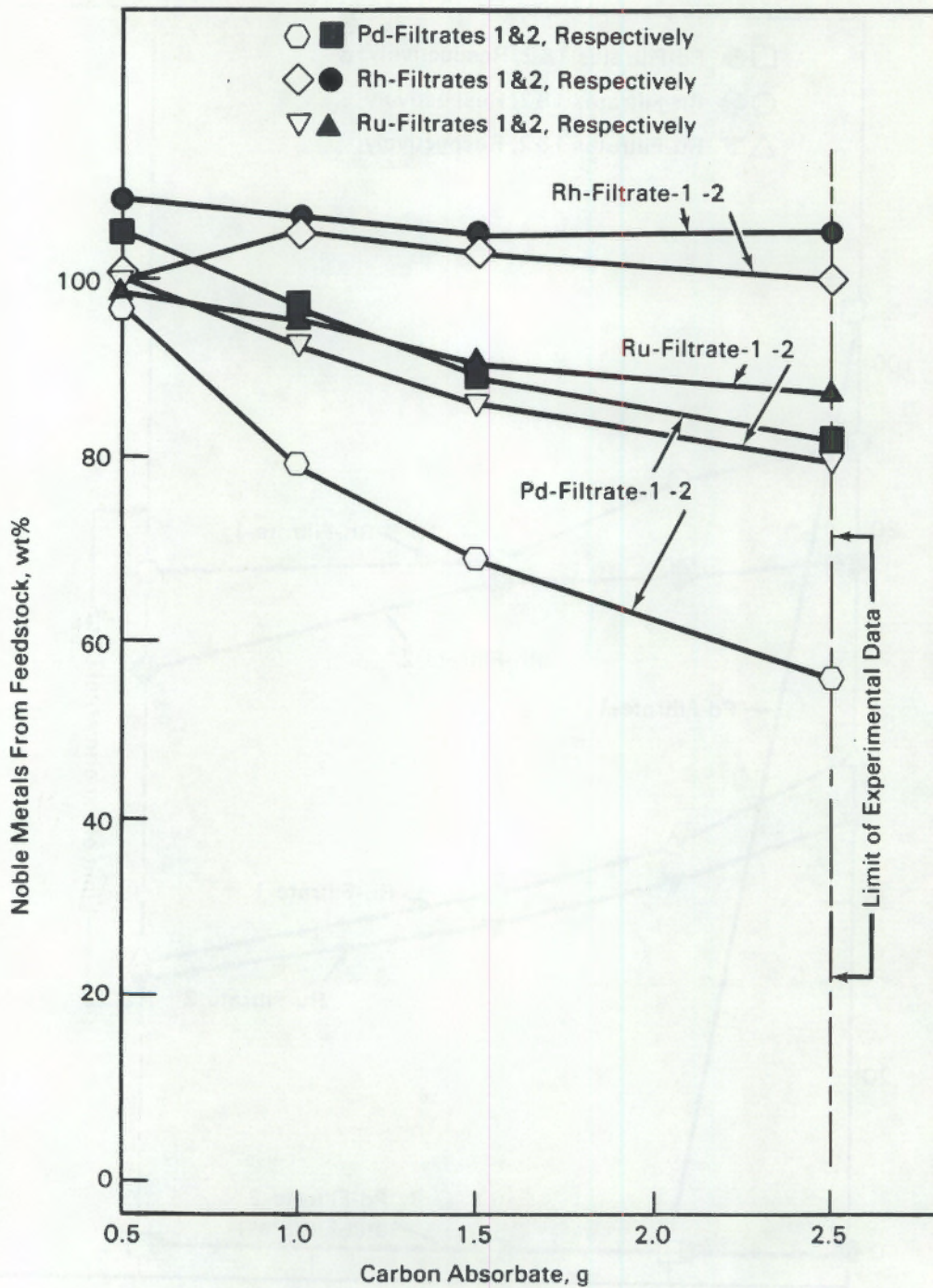


FIGURE 2. Noble Metals in Filtrates Following Contact of Commercial Simulated Waste by Chelate-Impregnated Activated Carbons

TABLE 3. Palladium in Filtrates Following Contact of Simulated Fuel Reprocessing Wastes with Chelate-Impregnated Carbon Adsorbents

Palladium in Feedstock

Simulated commercial waste: 428.3 mg/100mL

Simulated PUREX waste: 1.911 mg/100mL

Treatment	Carbon Adsorbent Used, g of Adsorbent/100 mL of Feedstock			
	0.5	1.0	2.0	2.5
	Pd Remaining in Filtrate, wt%(a)			
	Commercial Waste			
Carbon/DMG ^(b)	106 ^(d)	98	90	83.2
Carbon/PTU ^(c)	97.6	80.2	70.5	56.9
	PUREX Waste			
Carbon/DMG	106 ^(d)	0 ^(e)	0 ^(e)	0 ^(e)
Carbon/PTU	0 ^(e)	0 ^(e)	0 ^(e)	0 ^(e)

(a) Residual chelate-impregnated carbon adsorbent analyses uncertain; therefore, not listed.

(b) DMG - dimethylglyoxime used as chelate.

(c) PTU - phenylthiourea used as chelate.

(d) High value a result of analytical imprecision.

(e) Element content below analytical detection level (the limit of reliable measurement), about 0.05 µg/mL for each noble metal.

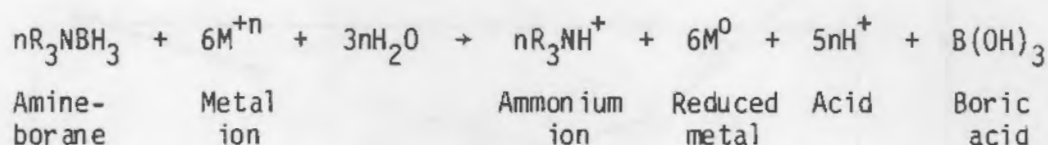
Further work needs to be conducted using chelate-impregnated carbon adsorbents to optimize operating conditions for maximum noble metal recoveries using adsorption columns and to prove the principles of the method using actual, radioactive waste solutions.

In batch flask-shaking tests of activated carbons, equilibrium conditions are soon reached between the absorbable substance attached to the carbon and that in solution; and no more will be removed. The advantage of using adsorption columns packed with carbon is that a solution partially depleted of the absorbable substance is continuously exposed to a fresher carbon adsorbent as it flows through the bed. This distribution relationship favors the carbon adsorbent, allowing it to become more fully loaded than in batch contact.

This condition exists until the carbon becomes exhausted and breakthrough of the adsorbable substance occurs into the column effluent. Significantly more noble metal should be removed from a test solution using adsorption columns rather than flasks.

AMINE-BORANE REDUCTIVE RESIN PROCESS EVALUATION

The use of hydride-containing reagents to reduce precious metals is well documented. One of the most common reagents used is sodium borohydride. Another reagent receiving attention is a class of compounds known as amine-boranes. Manziek (1982) states that amine-boranes are milder reducing agents and generally more selective than borohydrides and reports the potential of amine-borane reductive resins for removing palladium and other noble metals from solutions of their salts. The reducing reaction for the process can be illustrated as follows:



The specific resin evaluated in our screening tests was Amborane[®] 345, which was shown by Manziek to be reactive to palladium and rhodium. Details on the chemistry of these reactions are presented in Manziek (1982).

Small amounts (0.25 to 1.50 g) of the reductive resin were mixed in flasks with about 100 mL of simulated PUREX waste. The materials were shaken for 1 h at room temperature (-25°C) and filtered. The used resin and filtrate were then analyzed by ICP. Approximate noble metal recoveries from the simulated PUREX waste are shown in Figure 3 and Table B.3. No tests were made using simulated commercial waste. Recoveries of palladium from solution were satisfactory for the screening tests, but recoveries of rhodium and ruthenium were not. The poor ruthenium recovery was not unexpected (Manziek 1982), but more work is needed to identify reasons for the poor rhodium recovery. It is evident from the data that palladium recovery progressively increases with increase of the resin-to-waste solution ratio; these data are summarized in Table 4 and Figure 3.

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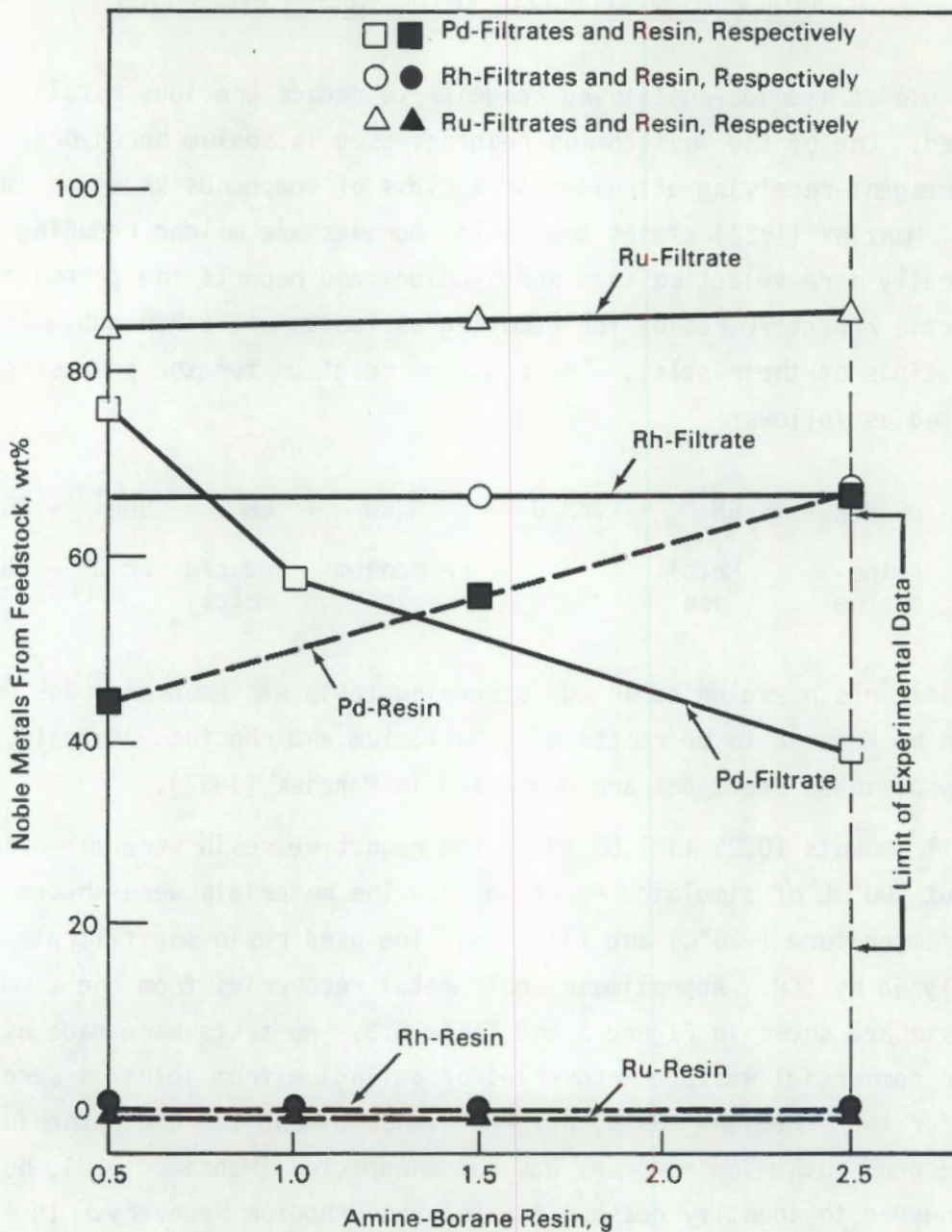


FIGURE 3. Noble Metal Distribution Following Contact of PUREX Simulated Waste by Amine-Borane Reductive Resin (1 h shaking)

Further testing with the amine-borane reductive resin focused on determining whether equilibrium had been reached and whether a longer contact time would result in more complete palladium recovery. Two simulated PUREX-type feedstocks were used. One had a palladium content nearly identical to that

TABLE 4. Palladium Recovery Using Amine-Borane Resins

Amine-borane resin, g/100 mL of feedstock	0.25	0.50	1.50
Pd recovery, wt% ^(a)	46	57	68

 (a) Percent recovery based on feedstock makeup weight.

used for the tests reported above; the second had a five-fold increase in the noble metal content. Amine-borane was used at 1.5 g/100 mL of waste solution. The tests revealed that increasing the contact time from 1 to 24 h reduced the recovery percentage rather than increased it (Table 5). With the more concentrated waste solution, the recovery decreased from about 50 wt% to 10 wt%. With the less concentrated waste solution, the recovery decreased from 68 wt% to 52 wt% (Table 8.3 data are included in Table 5 for comparison). This decrease corresponds to the decrease in Pd recovery from nitrate and HNO₃ solutions by amine-boranes over time reported by Manziek (1982; Figures 3, 5, and 9).

Palladium was quickly reduced and deposited on the amine-borane resin in this process. As the amine-borane is removed from the reaction, the reducing environment cannot be maintained and palladium is oxidized off the resin. Manziek also provides insight on the oxidation of palladium metal on the resin and shows the reaction to be a function of pH as well as time (Manziek 1982; p. 9-17 and Figure 5). Increasing the palladium concentration five-fold in simulated PUREX waste solution did not appear to have a substantial effect on the recovery fraction (5 mg from 9.96 mg Pd in the more-concentrated feedstock or 50 wt% recovery compared with 1.20 mg from 1.75 mg Pd in the less-concentrated feedstock or 68 wt% recovery).

A factor affecting the reliability of the amine-borane testing (as in the sugar and chelates testing) was the uncertain precision of the results on noble metal content in solid residues. This factor led to difficulty in comparing one test result with another and in interpreting the test results. It is speculated that the analytical difficulties may be due in part to representative sampling. The cause of these difficulties should be identified during future noble metal recovery process evaluation work.

TABLE 5. Noble Metal Recovery from Simulated Spent Fuel Reprocessing Wastes by Amine-Borane Reductive Resin - Test 2 (1 to 24 h shaking)

	Simulated Waste Type and Feedstock Code Number								
	PUREX Stock 2 Aliquot 2		PUREX Stock 2 Aliquot 2		PUREX Stock 2 Aliquot 1		PUREX Stock 1		
Feedstock noble metals, mg								(from Table A.3)	
Pd	9.96		9.96		1.911		1.753		
Rh	10.35		10.35		2.587		2.587		
Ru	50.00		50.00		10.0		10.00		
Shake time, h	1		24		24		1		
Amine-borane resin, g	1.5		1.5		1.5		1.5		
Noble metal distribution	mg	wt%	mg	wt%	mg	wt%	mg	wt%	
Pd in resin	5.00	50.2	1.00	10.0	1.00	52.3	1.200	68.4	
Pd in filtrate	--	--	6.25	62.8	--	--	0.724	41.3	
Rh in resin	<0.05	<0.5	0.070	0.7	0.070	2.7	<0.06	<2	
Rh in filtrate	9.66	97.0	9.66	97.0	2.42	93.5	2.42	68	
Ru in resin	0.45	0.9	0.63	1.3	0.280	2.8	<0.07	<0.7	
Ru in filtrate	41.9	83.8	38.6	77.2	6.90	69.0	8.72	87	

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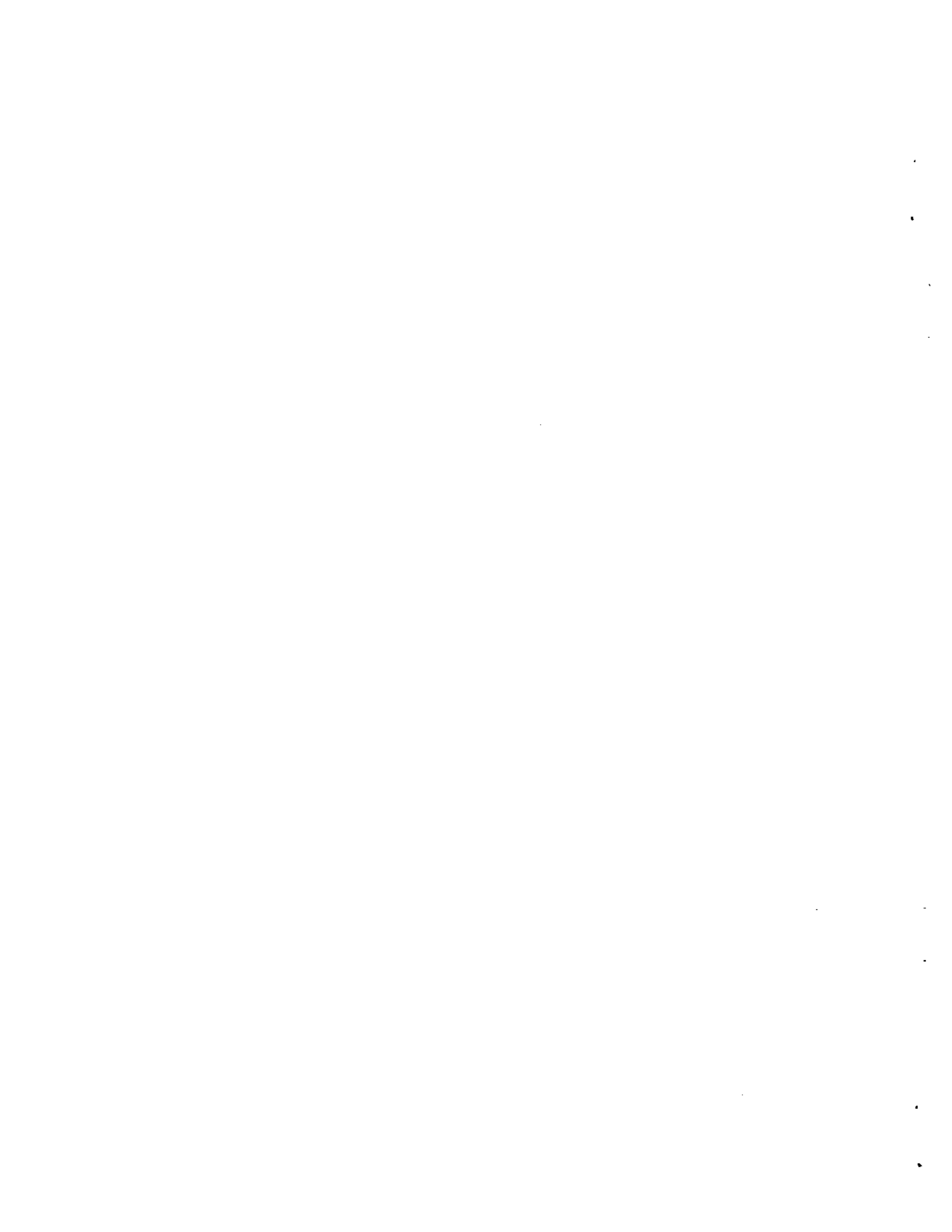
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APPENDIX A

PRECISION OF ICP ANALYSES FOR NOBLE METALS
IN SIMULATED WASTE TEST FEEDSTOCKS

APPENDIX A

PRECISION OF ICP ANALYSES FOR NOBLE METALS
IN SIMULATED WASTE TEST FEEDSTOCKS

Table A.1 compares the noble metal contents of simulated waste test feedstocks determined by analytical balance and volumetric transfer measurements with the results of ICP analyses. The ranges, means, and standard deviations for the percent differences of the ICP analyses from the feedstock noble metal makeup values are given below:

	<u>Range, Difference from Makeup Value, %</u>	<u>Mean, %</u>	<u>Standard Deviation, %</u>
Pd	-12 to 20	0.87	8.6
Rh	0.6 to 5.5	4.0	1.9
Ru	-0.25 to 15	4.56	4.7

TABLE A.1. Comparison of Feedstock Makeup^(a) and ICP Analyses

Simulated Waste Type and Feedstock Code No.	Pd, mg/mL		Rh, mg/mL		Ru, mg/mL	
	Make up	ICP	Make up	ICP	Make up	ICP
PUREX 1, blank	0	0	0	0	0	0
PUREX 2, blank	0	0	0	0	0	0
Commercial 1, blank	0	0	0	0.0026	0	0.005
PUREX 2, Aliquot 1	0.0182	0.016	0.02464	0.026	0.09524	0.096
% difference ^(b)		-12		5.5		0.80
PUREX 2, Aliquot 2	0.09846	0.096	0.09855	0.104	0.4762	0.475
% difference		-2.5		5.5		-0.25
PUREX 2, Aliquot 3	0.1897	0.186	0.1971	0.200	0.9524	0.980
% difference		-2.0		1.5		2.9
Commercial 1, Aliquot 1	3.747	3.575	0.9053	0.911	5.249	5.510
% difference		-4.6		0.63		5.0
PUREX 1	0.01669	0.020	0.02464	0.026	0.09524	0.110
% difference		20		5.5		15
HNO ₃ & PUREX Aliquot 1 noble metals	0.0182	0.018	0.02464	0.026	0.09524	0.099
% difference		-0.1		5.5		3.9
HNO ₃ & PUREX Aliquot 2 noble metals	0.09486	0.097	0.09855	0.102	0.4762	0.485
% difference		2.3		3.5		1.8
HNO ₃ & PUREX Aliquot 3 noble metals	0.1897	0.194	0.1971	0.204	0.9524	0.984
% difference		2.3		3.5		3.3
HNO ₃ & Commercial Aliquot 1 noble metals	3.747	3.920	0.9053	0.953	5.249	5.700
% difference		4.6		5.3		8.6
% Difference						
Mean		0.87		4.0		4.6
Standard deviations		8.6		1.9		4.7

(a) Weights determined from analytical balance and volumetric transfer measurements.
(b) % difference of ICP analyses from makeup values.

APPENDIX B

DATA FOR CHELATE-IMPREGNATED CARBON ADSORBENT
AND AMINE-BORANE REDUCTIVE RESIN TESTS

APPENDIX B

DATA FOR CHELATE-IMPREGNATED CARBON ADSORBENT AND AMINE-BORANE REDUCTIVE RESIN TESTS

Tables B.1 and B.2 show data for recovery of noble metals by chelate-impregnated carbon adsorbents from simulated PUREX and commercial spent fuel reprocessing wastes. Table B.3 shows similar data for noble metal recovery using an amine-borane reductive resin.

TABLE B.1. Noble Metal Recovery from Simulated Spent Fuel PUREX Reprocessing Wastes by Selected Chelates Deposited on Activated Carbon

	Simulated Waste Type and Feedstock Code Number							
	PUREX		PUREX		PUREX		PUREX	
	Stock 2	Aliquot 1	Stock 2	Aliquot 1	Stock 2	Aliquot 1	Stock 2	Aliquot 1
Feedstock noble metals, mg ^(a)								
Pd	1.911		1.911		1.911		1.911	
Rh	2.587		2.587		2.587		2.587	
Ru	10.0		10.0		10.0		10.0	
Activated carbon and chelate, g	0.5		1.0		1.5		2.5	
Noble metal distribution ^(b)	mg	wt%	mg	wt%	mg	wt%	mg	wt%
1st Chelate: DMG								
Pd in filtrate	2.03	106	(c)	--	(c)	--	(c)	--
Rh in filtrate	2.34	90.5	2.24	86.6	2.00	77.3	1.98	76.5
Ru in filtrate	5.63	56.3	4.64	46.4	4.01	40.1	3.17	31.7
2nd Chelate: PTU								
Pd in filtrate	(c)	--	(c)	--	(c)	--	(c)	--
Rh in filtrate	2.05	79.2	2.02	78.1	1.94	74.9	1.66	64.2
Ru in filtrate	4.89	48.9	4.21	42.1	3.72	37.2	3.12	31.2

(a) Weights determined from analytical balance and volumetric transfer measurements. The number of decimal places shown are for future data tracking and do not indicate accuracy of measurements.

(b) Weights determined from ICP analyses.

(c) Analysis made; element content below detection level.

Activated carbon: Norit 14 x 60 granular carbon, American Norit Co., Jacksonville, Florida.

DMG (dimethylglyoxime), J. T. Baker Chemical Company, Phillipsburg, New Jersey.

PTU (1 phenyl 2 thiourea), Eastman Kodak Company, Rochester, New York.

Code numbers are shown in tables of this report to permit easy return to original data for use in future work.

TABLE B.2. Noble Metal Recovery from Simulated Spent Fuel Commercial Reprocessing Wastes by Selected Chelates Deposited on Activated Carbon

	Simulated Waste Type and Feedstock Code Number							
	Commercial		Commercial		Commercial		Commercial	
	Stock	Aliquot	Stock	Aliquot	Stock	Aliquot	Stock	Aliquot
Feedstock noble metals, mg								
Pd	428.3		428.3		428.3		428.3	
Rh	103.5		103.5		103.5		103.5	
Ru	600		600		600		600	
Activated carbon and chelate, g	0.5		1.0		1.5		2.5	
Noble metal distribution	mg	wt%	mg	wt%	mg	wt%	mg	wt%
1st Chelate: DMG								
Pd in filtrate	453.0	106	419.8	98.0	385.5	90.0	356.2	83.2
Rh in filtrate	114.4	110.5	111.9	108.1	109.4	105.7	111.0	107.2
Ru in Filtrate	596.0	99.3	583.0	97.2	547.1	91.2	534.2	89.0
2nd Chelate: PTU								
Pd in filtrate	418.2	97.6	343.3	80.2	302.0	70.5	243.6	56.9
Rh in filtrate	104.6	101.1	110.2	106.5	107.4	103.8	104.1	100.6
Ru in filtrate	601.2	100.2	561.2	93.5	523.3	87.2	487.2	81.2

TABLE B.3. Noble Metal Recovery from Simulated Spent Fuel Reprocessing Wastes by Amine-Borane Reductive Resin - Test 1 (1 h shaking)

	Simulated Waste Type and Feedstock Code Number					
	PUREX Stock 1		PUREX Stock 1		PUREX Stock 1	
Feedstock noble metals, mg						
Pd	1.753(a)	(2.100)(b)	same	same	same	same
Rh	2.587(a)	(2.730)(b)	same	same	same	same
Ru	10.00(a)	(11.55)(b)	same	same	same	same
Amine-borane resin, g	0.25		0.50		1.50	
Noble metal distribution(b,c)	mg	wt%	mg	wt%	mg	wt%
Pd in resin	0.800	45.6 (38)(d)	1.00	57.0 (48)(d)	1.200	68.4 (57)(d)
Pd in filtrate	1.365	77.9	1.029	58.7	0.724	41.3
Rh in resin	<0.06	<2	<0.06	<2	<0.06	<2
Rh in filtrate	2.52	68	2.52	68	2.42	68
Ru in resin	<0.06	<0.6	<0.06	<0.6	<0.07	<0.7
Ru in filtrate	8.61	86	8.72	87	8.72	87

(a) Feedstock makeup weights determined by analytical balance and volumetric transfer measurements.

(b) Weights determined from ICP analyses.

(c) Percent recovery based on feedstock makeup weight.

(d) Percent recovery based on ICP analyses of feedstock.

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