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RECOVERY OF PALLADIUM FROM NUCLEAR WASTE SOLUTIONS
USING A PACKED COLUMN OF TRICAPRYL MONOMETHYL
AMMONIUM CHLORIDE ON AN INERT SUPPORT

By

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ABSTRACT

Palladium is present in supernatant solutions in the high-salt wastes which have been stored following the recovery of actinides from irradiated uranium.

A particular means to isolate palladium from waste solutions has been demonstrated. Palladium is preferentially retained on a packed column of Aliquat-336* (tricapryl monomethyl ammonium chloride) fixed on an inert support. A homogeneous powder, uniformly coated with the amine extractant, is prepared by dissolving Aliquat-336 in xylene, mixing with Plaskon** (a trifluorochloroethylene polymer), and volatilizing the xylene. The powder, mixed with asbestos (flow rate aid), was packed in an 8 mm column. High-salt basic waste solution was passed through the column until 50 percent palladium breakthrough was achieved, resulting in 13.3 mg of palladium present on the 446 mg of Aliquat-336.

Elution was accomplished by cycles of 8.0M HNO_3 and 1.5M NH_4OH . The first cycle of 8.0M HNO_3 resulted in the recovery of 55 percent of the palladium in 35 ml of eluent (0.22 g/liter Pd). The first cycle of 1.5M NH_4OH recovered an additional 25 percent in 30 ml of eluent. The total recovery of palladium from the column in three complete elution cycles was 97 percent.

Effective separation of the palladium from rhodium was evident.

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AMMONIUM CHLORIDE ON AN INERT SUPPORT

INTRODUCTION

Palladium and rhodium are among those elements produced in highest yield in the fission process. The low radioactivity of these particular fission products opens possibilities for supplementing natural sources of the valuable metals.

The world is dependent upon South Africa, Russia, and Canada for natural sources of palladium and rhodium. The demand for these rare metals is increasing as natural reserves are shrinking. Studies indicate that by 1978, annual rhodium formation in United States power reactor fuels will equal the quantity that is currently consumed by the United States in an average year. A similar situation will exist for palladium by about 1990.⁽¹⁾

The current price of rhodium is more than five times that of palladium, which places greater emphasis on separation and recovery of rhodium. This study describes a method designed to conveniently separate palladium from the system, thus simplifying the recovery of rhodium, and at the same time allowing the isolation and recovery of palladium. A report by Panesko⁽²⁾ describes a proposed recovery process for rhodium. His report also includes provisions for the recovery of technetium, which is present in recoverable amounts, and palladium.

Since palladium is the principal concern of this report, Table I is presented to indicate isotopic compositions of natural and probable fission product palladium from power reactors.

TABLE I
ISOTOPIIC COMPOSITION COMPARISON OF NATURAL
AND FISSION PRODUCT PALLADIUM⁽³⁾

<u>Isotope</u>	<u>Natural %</u>	<u>Fission Product %</u>
¹⁰² Pd	0.96	
¹⁰⁴ Pd	10.97	1
¹⁰⁵ Pd	22.23	49
¹⁰⁶ Pd	27.33	22
¹⁰⁷ Pd*	None	16
¹⁰⁸ Pd	26.71	9
¹¹⁰ Pd	11.81	3

* Radioactive (7×10^6 year half-life, 0.035 Mev beta, no gamma).

Although ¹⁰⁷Pd is radioactive, the activity is extremely low, as is the energy of the beta particle. This, coupled with the fact that palladium is an inert and biologically-unreactive element, leaves little concern about the use of fission product palladium in industry. Palladium is used mainly in the electrical, chemical, and medical-dental fields. The principal use of palladium in the electrical industry is in contact points for low-voltage switch gear. In the chemical industry, it is used in hydrogen purification and as a catalyst.

SUMMARY

A particular means to isolate palladium from waste solutions for rhodium recovery has been demonstrated. Palladium is preferentially retained on a packed column of Aliquat-336 (tricapryl monomethyl ammonium chloride) fixed on an inert support.

Approximately 2,400 ml of basic waste solution (0.01 g/liter Pd, 0.01 g/liter Rh) were passed through an 8 mm glass column containing 2.8 ml of a mixture of Aliquat-336 on the inert support and asbestos (flow rate aid) before 50 percent breakthrough. At 50 percent breakthrough, 13.3 mg of palladium were present on the 446 mg of Aliquat-336 contained in the column. The column effluent contained the rhodium.

Cyclic elution with 8.0M HNO_3 and 1.5M NH_4OH was used to recover the palladium. The first cycle of 8.0M HNO_3 resulted in the recovery of 55 percent of the palladium in 35 ml of eluent (0.22 g/liter Pd). The rhodium content was 0.0026 g/liter. The first cycle of 1.5M NH_4OH recovered an additional 25 percent in 30 ml of eluent (0.11 g/liter Pd). Rhodium was not detectable.

An additional 11 percent palladium was recovered with a complete second cycle, with 6 percent being recovered by a third complete cycle. The total recovery of palladium from the column was 97 percent for three elution cycles.

EXPERIMENTAL MATERIALS

ALIQUAT-336 (General Mills, Inc., Kankakee, Illinois) is a water-insoluble quaternary mixture of C_8 and C_{10} carbon chains with C_8 predominating. The suggested chemical compound is tricaprlyl monomethyl ammonium chloride. The compound is a highly-viscous liquid with an average molecular weight of 442 and a specific gravity of 0.884 $\frac{25^\circ\text{C}}{25^\circ\text{C}}$.

PLASKON (Allied Chemical, Morristown, New Jersey), type CTFE 2300, is a trifluorochloroethylene polymer and comes as a fine, white powder.

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A procedure reported by Huff⁽⁴⁾ was followed for bonding Aliquat-336 to Plaskon to form a solid ion exchange packing material. A 50 wt percent solution of Aliquat-336 in xylene was made. Equal weights of the solution and Plaskon were stirred until uniform. This mixture was kept at 70 C until a constant weight was attained--the weight loss being equivalent to complete volatilization of the xylene diluent. The resultant product was a homogeneous powder that appeared to be uniformly coated with the amine extractant.

COLUMN PACKING

An 8 mm column was packed to a volume of 2.8 ml with the prepared adsorbent mixed with asbestos. The Gooch Grade asbestos, which occupied 40 percent of the volume, was used to give porosity to the column and thus increase flow rate. The column contained 446 mg of tricapryl monomethyl ammonium chloride.

STABILITY OF PACKING

The material showed excellent stability as to bonding between the extractant and the inert support. Approximately 7 percent of the extractant was easily washed off with water, while the remainder was very well bonded. Alkaline feed and eluting agents did not cause significant removal of the extractant.

ANALYTICAL

Atomic absorption methods were used for the determination of palladium and rhodium.

Tricapryl monomethyl ammonium chloride was determined by recording spectrophotometer in the near-infrared region (2.97 microns) using carbon tetrachloride as the diluent. (5)

FEED SOLUTION AND COLUMN LOADING

Waste solutions generated by processes involving recovery of actinides from irradiated uranium are made alkaline and stored for years in huge underground tanks. The feed material used in this study was supernatant solution from these stored high-salt wastes after cesium removal.

Table II presents the approximate composition of the feed solution.

TABLE II
APPROXIMATE FEED SOLUTION

Na ⁺	5 <u>M</u>	Rh	0.01 g/liter
NO ₃ ⁻	0.5 <u>M</u>	Pd	0.01 g/liter
NO ₂ ⁻	2 <u>M</u>	Tc	0.02 g/liter
CO ₃ ⁼	1 <u>M</u>		
SO ₄ ⁼	0.3 <u>M</u>	pH	11-12

Approximately 2,400 ml of the feed solution were passed through the column at rates 0.2 to 0.5 ml/min. At 50 percent breakthrough, 13.3 mg of palladium were present on the column. A color photograph of the loaded column (50 percent breakthrough) is attached (page 10).

ELUTION

Preliminary runs, involving synthetic solutions in which reagent grade Pd(NO₃)₂ was used, indicated good loading

characteristics and excellent elution with 1.5M ammonium hydroxide. Analytical work by Campbell⁽⁶⁾ had indicated that 1.5M ammonium hydroxide may prove effective. An initial run involving process solution indicated that only 3.3 percent of the loaded palladium was eluted by 1.5M NH_4OH .

It is known that palladium species formed in process solutions are much different from that involved in simple laboratory makeup. Several species of nitrogen-oxygen complexes are thought to occur in process solutions for both palladium and rhodium. Considerable work has been done by Hoffman⁽⁷⁾ to identify the rhodium species. Identification of the palladium species remains to be done.

It was found that 8.0M HNO_3 would elute considerable palladium as well as affect a change in much of that left on the column, so that 1.5M NH_4OH could be used to elute the new species. Thus a cyclic system of elution was developed as indicated in Table III, page 7. Note that wash solutions were used between acid and base additions to avoid heat generation and to better define the elution characteristics of each solution.

The three elution cycles resulted in a palladium recovery of 97 percent. All acidic solutions were made basic with NH_4OH , after elution, to avoid precipitation of palladium compounds with time.

TEMPERATURE

Loading and elution were accomplished at approximately 25 C. Scouting runs indicated that benefits from temperatures in excess of 25 C were negligible.

TABLE III
ELUTION OF PALLADIUM FROM LOADED COLUMN

<u>Solution</u>	<u>Volume</u> ml	<u>Palladium</u>		<u>Rhodium</u> mg
		mg	% Recovery	
0.1M HNO ₃	60	<0.05		
<u>Cycle 1</u>				
8.0M HNO ₃	5	3.825		0.055
8.0M HNO ₃	5	1.620		0.025
8.0M HNO ₃	5	0.865		<0.01
8.0M HNO ₃	5	0.530		
8.0M HNO ₃	5	0.340		
8.0M HNO ₃	5	0.210	55.6	
H ₂ O	5	0.074		
H ₂ O	5	<0.005	0.6	
1.5M NH ₄ OH	5	2.520		<0.01
1.5M NH ₄ OH	5	0.510		<0.01
1.5M NH ₄ OH	5	0.159		
1.5M NH ₄ OH	5	0.056		
1.5M NH ₄ OH	5	0.041	24.7	
H ₂ O	5	0.022	0.2	
<u>Cycle 2</u>				
8.0M HNO ₃	5	0.310		
8.0M HNO ₃	5	0.342		
8.0M HNO ₃	5	0.180		
8.0M HNO ₃	5	0.115	7.1	
H ₂ O	5	0.040	0.3	
1.5M NH ₄ OH	5	0.349		
1.5M NH ₄ OH	5	0.075		
1.5M NH ₄ OH	5	0.042		
1.5M NH ₄ OH	5	0.011	3.6	
H ₂ O	5	<0.005		
<u>Cycle 3</u>				
12.0M HNO ₃	5	0.210		
12.0M HNO ₃	5	0.175		
12.0M HNO ₃	5	0.135		
12.0M HNO ₃	5	0.065	4.4	
H ₂ O	10	<0.005		
1.5M NH ₄ OH	5	0.151		
1.5M NH ₄ OH	5	0.035		
1.5M NH ₄ OH	5	0.010		
1.5M NH ₄ OH	5	0.007	1.5	
H ₂ O	10	<0.005		

PURIFICATION

Additional purification and concentration of palladium, involving $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ and palladium dimethylglyoximate precipitation steps have been developed by Panesko.⁽⁸⁾

ACKNOWLEDGMENTS

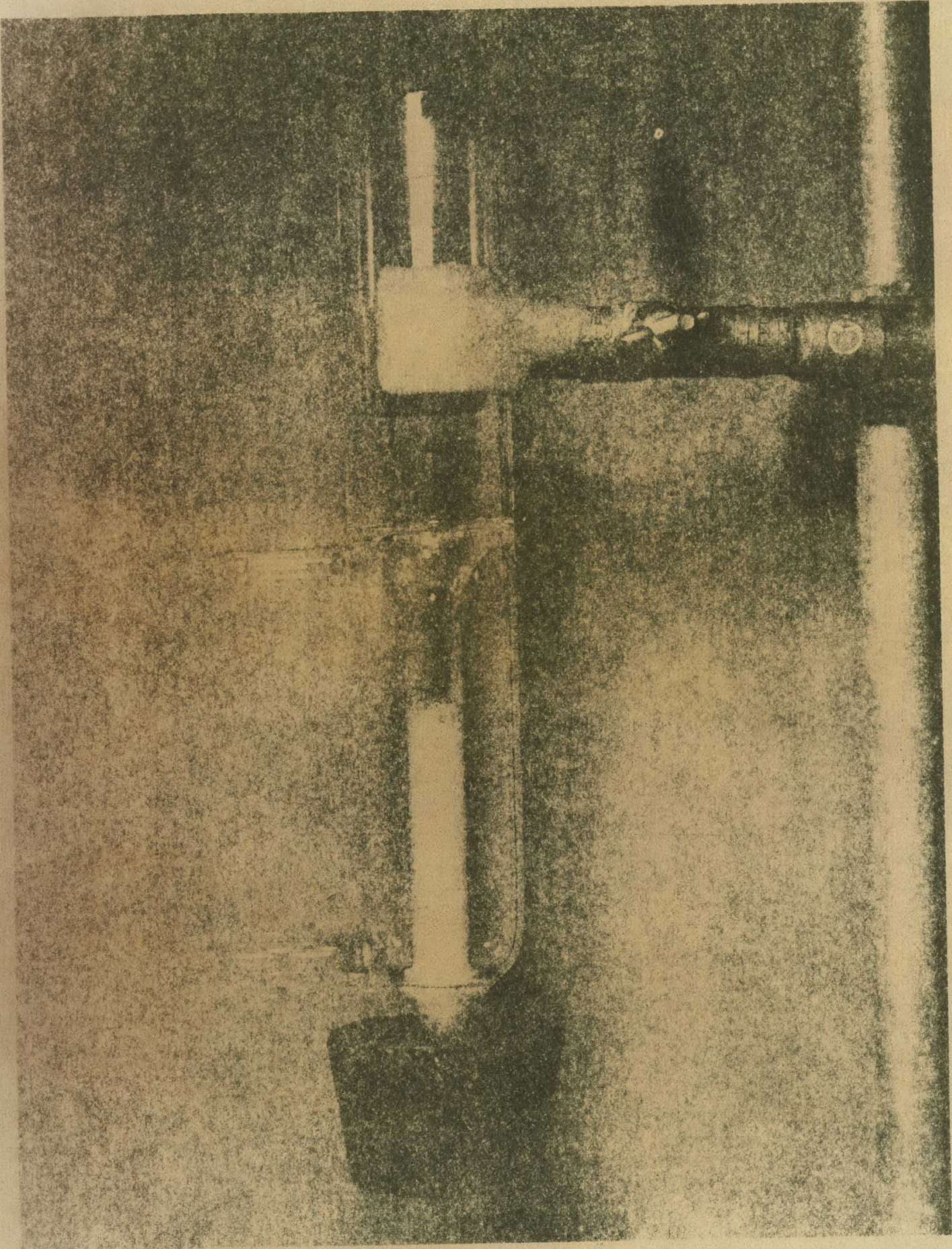
The author appreciates the technical suggestions of M. H. Campbell and J. V. Panesko involved in planning this project.

The laboratory work performed by J. E. Horton and A. O. Anderson is also very much appreciated.

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H ₂ O	10	<0.005		

PURIFICATION

Additional purification and concentration of palladium, involving $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ and palladium dimethylglyoximate precipitation steps have been developed by Panesko.⁽⁸⁾

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