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FISSION PRODUCT RHODIUM AND PALLADIUM

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FISSION PRODUCT RHODIUM AND PALLADIUM

Interim Report

F. P. Roberts

INTRODUCTION

The evaluation of fission product rhodium and palladium as substitutes in industry for the natural elements is underway at PNL. The first phase of this study is to determine the nature and amount of radioactivity associated with these fission products and to assess the problems which may be encountered with their use.

Of all the inert (non-radioactive) fission products only rhodium and palladium appear to have sufficient value to warrant recovery. These will have value only if they are sufficiently free of radioactive constituents to permit relatively unrestricted use at the present value ($\sim$ \$8.00 and \$1.40 per gram of rhodium and palladium respectively). We believe rhodium or rhodium and palladium can be recovered at costs competitive with the naturally occurring elements.

Fission product rhodium consists mainly of stable ^{103}Rh . Two other isotopes are known to exist which may be formed by multiple neutron emissions from ^{103}Rh . These are ^{101}Rh (3.1 y) and ^{102}Rh (205 d and 2.9 y). The ^{102}Rh has two isomers. All decay with the emission of penetrating gamma rays and, if present in large amounts, will complicate the exploitation of fission product rhodium.

Fission product palladium consists of ^{105}Pd , ^{106}Pd , ^{107}Pd , ^{108}Pd , and ^{110}Pd . Of these only ^{107}Pd is radioactive. Although ^{107}Pd is about 20% of the total, it has such a long half-life (7×10^6 y) and decays by such a low

energy beta (0.035 Mev) that no dose problems from its presence will be noted and we believe that it will not prevent industrial use of fission product palladium. This study does include the search for gamma emitting palladium isotopes which may have gone undetected in the past.

SUMMARY

Milligram quantities of fission product rhodium separated from spent fuel from Yankee and Hanford reactors have been analyzed for the ^{102m}Rh and ^{102}Rh content. At discharge the ^{102m}Rh content was estimated to be 290 $\mu\text{Ci/g}$ Rh for the 33,000 MWd/t Yankee sample and 20 $\mu\text{Ci/g}$ Rh for the Hanford samples.

Samples of palladium separated from the Yankee fuel showed no gamma ray emission.

EXPERIMENTAL

The measurement of gamma emitting isotopes in the fission product rhodium and palladium requires a carrier-free isolation and purification procedure capable of giving very high decontamination from other radioactive constituents in the sample. High yields are not necessary, but because of the limited size of available samples 10-50% recovery is desirable. Other workers have shown that rhodium can be separated from uranium by precipitation of the metal⁽¹⁾ and sulfide⁽²⁾, and there are numerous radiochemical purification procedures. These have been collected in an excellent review by Armstrong and Choppin.⁽³⁾ The procedure used here is a combination of several of these.

1. Samples

Three sources of fission products were available for study in Fiscal Year 1969.

1. A Yankee sub-assembly consisting of UO_2 clad in stainless steel. The fuel had been irradiated to an average of 35,000 MWd/t and discharged in August, 1965.

2. Purex high level waste resulting from the processing of normal production Hanford fuel in Purex Plant. This solution contains little uranium or plutonium but does contain gross amounts of iron and aluminum. The fission products in this sample were aged 1 year.
3. A sample of purified rhodium recovered from 11-year-old Hanford alkaline waste. This material had been recovered by an anion exchange process⁽⁴⁾ and made available to us by Atlantic Richfield Hanford Company.

2. Isolation of Rhodium and Palladium from Yankee Fuel

The fuel rods from the Yankee sub-assembly were cut in one-inch sections. Samples of these sections were treated with warm 8M HNO_3 to leach the UO_2 and leave the stainless steel cladding intact. After leaching the cladding was discarded and the solution containing the fuel was boiled to near dryness to remove the excess HNO_3 . After dilution to a known volume a sample was taken to use for the burnup determination. The rhodium and palladium were precipitated from the remaining solution with hydrogen sulfide. The sulfides were dissolved in aqua regia. Because the sulfide precipitation carries ruthenium, silver, antimony, and tellurium, as well as rhodium and palladium, further separations were needed. The ruthenium was removed by distillation from H_2SO_4 - HClO_4 solution and the antimony by distillation from a H_2SO_4 -HBr solution. Finally the rhodium and palladium were precipitated as iodides. Decontamination at this point was sufficient to allow removal from the high-level cell for final purification.

3. Isolation of Rhodium from Purex High Level Waste

A different procedure was used to isolate the rhodium from the Purex waste solution because of the much lower concentration of rhodium. The procedure used does not recovery palladium. In this procedure the Purex acid waste solution (after centrifuging to remove solids) was made strongly basic to

precipitate the iron as $\text{Fe}(\text{OH})_3$, which carries rhodium. The supernate, which was discarded, contains the aluminum and cesium. The $\text{Fe}(\text{OH})_3$ precipitate was dissolved in HNO_3 , made 1.0M in NaNO_2 , and boiled to convert rhodium into the soluble nitrite complex and the pH adjusted to about 7. The $\text{Fe}(\text{OH})_3$ precipitate carries the bulk of the fission products and was discarded. The supernate containing the rhodium was made 1M in potassium by adding potassium nitrite and heated to form the insoluble potassium rhodinitrite. This precipitate was dissolved in hydrochloric acid and reprecipitated as potassium rhodinitrite. At this point it was decontaminated sufficiently to remove from the high level cell for final purification.

4. Final Purification and Separation of Rhodium from Palladium

The products from the steps described in the preceding paragraphs contained $^{110\text{m}}\text{Ag}$, ^{125}Sb , ^{106}Ra , ^{137}Cs , ^{134}Cs , as well as minor amounts of other fission products. Further decontamination was required, and the rhodium and palladium had to be separated.

The distillation of ruthenium and antimony was repeated using inert carriers. This was followed by conversion of the rhodium and palladium to soluble nitrite complexes and performing a series of $\text{Fe}(\text{OH})_3$ scavenges with silver and antimony carriers. The rhodium was then precipitated and recovered as potassium rhodinitrite. The supernate was acidified, and the palladium was precipitated as palladium dimethylglyoximate.

The rhodium product contained no detectable radioactive impurities but the palladium contained traces of ^{125}Sb . To remove this the dimethylglyoxime precipitate was dissolved and the precipitation repeated until no gamma activity could be detected.

5. Rhodium and Palladium Assay

The total weight of rhodium recovered was determined by the spectrophotometric method based on the color formed on reaction of rhodium with stannous

iodide⁽⁵⁾. The palladium was determined by weighing the dimethylglyoximate precipitate.

6. Burn-Up Measurement

The estimates of burn-up in the Yankee samples were obtained by measurement of ¹³⁷Cs content.

7. Counting Methods

The isotopic compositions of the purified rhodium samples were determined by gamma energy analysis using a high resolution Ge(Li) detector in conjunction with a multi-channel pulse height analyzer. The samples in aqueous solution were counted as long as was required to accumulate at least 5000 counts in the photopeaks of interest.

The gamma energy spectra from the decay of ^{102m}Rh and ¹⁰²Rh have differences which permit the determination of both. The gamma energies and yields are shown in Table I. Figure I gives a graphic display showing the differences between well-aged and "green" rhodium.

The search for gamma rays from the palladium samples was done both with the Ge(Li) detector and a much more efficient 3 x 3 in NaI(Tl) crystal.

TABLE I

GAMMA RAY ENERGIES AND YIELDS OF ¹⁰²Rh AND ^{102m}Rh (6)

<u>Energy, Kev</u>	<u>Yield, Number of Gammas Per Decay</u>	
	<u>¹⁰²Rh (206 d half-life)</u>	<u>^{102m}Rh (2.9 y half-life)</u>
418.5	None	0.13
475.2	0.57	0.95
511.0	0.25	None
632.0	0.04	.54
698.1	None	0.41
768.3	None	0.30
1046.9	None	0.41
1102.7	0.03	0.05
1111.7	None	0.22
1370	0.005	None
1570	0.002	None

RESULTS

1. Rhodium Composition

The measured values obtained for the ^{102}Rh and $^{102\text{m}}\text{Rh}$ content of Yankee and Hanford samples are shown in Table II. Also shown are the values corrected for decay back to the reactor discharge date based on half-lives of 205 d and 2.9 years for ^{102}Rh and $^{102\text{m}}\text{Rh}$, respectively. (6)

TABLE II
COMPOSITION OF FISSION PRODUCT RHODIUM

<u>Source</u>	<u>Burn-Up MWd/T</u>	<u>Isotopic Composition $\mu\text{Ci/g Rh}$</u>			
		<u>^{102}Rh</u>	<u>$^{102\text{m}}\text{Rh}$</u>	<u>^{102}Rh</u>	<u>$^{102\text{m}}\text{Rh}$</u>
Yankee	33,000	25 ± 10	120 ± 25	1900 ± 700	280 ± 60
Yankee	33,000	25 ± 10	130 ± 25	1900 ± 700	300 ± 60
Yankee	37,000	35 ± 10	180 ± 40	2600 ± 1000	420 ± 90
Hanford, 1 year old		19.3 ± 5	7.2 ± 2	85 ± 20	9.6 ± 3
Hanford, 12 years old		not detectable	1.7 ± 0.5	---	30 ± 9

The three values obtained from the Yankee samples are in satisfactory agreement. The difference between the first and second sample and the third sample is not surprising because of the rather large difference in burn-up.

The difference in the $^{102\text{m}}\text{Rh}$ content of the 1-year-old and 12-year-old Hanford sample is greater than expected and is not readily explainable. The uncertainty of the published half-life is ± 0.9 year, but even so it does not account for the difference observed here. Additional work is required to elucidate this point and its possible implications.

2. Composition of Palladium

The only long lived radioactive isotope of palladium which might be formed in a reactor is ^{107}Pd . This isotope decays by emission of a 0.04 Mev beta

and no gamma. (6) A total of 22 mg of palladium recovered from the three Yankee samples was counted for extended periods in search of gammas in the energy region of 0.04 - 2.0 Mev. None were found. Based on the detection limits of the counter, we find there is less than 5×10^{-2} $\mu\text{Ci/g}$ Pd of any discrete gamma associated with the fission product palladium.

3. Dose Rates from Fission Product Rhodium

Fission product rhodium contains significant amounts of ^{102}Rh and ^{102m}Rh at short and intermediate cooling times. The fabrication and use of devices containing massive amounts of the rhodium will require some special handling to protect workers from potential hazards from the radiation.

Some calculations have been made to illustrate the magnitude of the radiation doses and are described here:

Case I. For the first case a 1 Kg source of rhodium in the form of a right cylinder containing 81 cm^3 and a density of 12.4 was assumed. The height and diameter were equal.

Case II. Because many applications for rhodium are as alloys with platinum, a source similar to Case I was constructed using an alloy containing 1 Kg of 90% Pt - 10% Rh.

Case III. The largest single industrial application for rhodium is the catalyst beds used in nitric acid plants. For Case III we assumed a catalyst bed for a 300 ton/day plant containing 20 Kg 90% Pt - 10% Rh. This bed is fabricated of layers of 80 mesh weave 0.003 inches thick. The shape is that of a hexagon 54 inches on the diagonal.

The dose rates for these three cases were calculated by the computer program developed by Malenfort. (7) The composition of the rhodium at the time of reactor discharge used in the calculations are given in Table III.

TABLE III
RHODIUM COMPOSITION USED IN DOSE RATE CALCULATIONS

	<u>Amount at Discharge</u>	
	<u>Yankee</u>	<u>Hanford</u>
^{102}Rh	1900 $\mu\text{Ci/g Rh}$	85 $\mu\text{Ci/g Rh}$
^{102m}Rh	290 $\mu\text{Ci/g Rh}$	20 $\mu\text{Ci/g Rh}$

Table IV gives the calculated dose rate for various cooling times at one foot and one meter from the source. Also, the data for the catalyst bed is depicted in Figure 2. The non-linearity of the curves at short cooling time is the effect of the decay of the short lived ^{102}Rh .

It is evident that for some industrial applications the fission product will require some "aging" before it can be used without restrictions. The length of the "aging" period will be determined by the allowable dose rates which will have to be established for each specific application and will depend on such factors as the amount of handling, the proximity to plant workers, the amount of shielding which can be tolerated, etc.

The amount of radioactivity associated with the Hanford rhodium is 7% that of the Yankee rhodium. In terms of the amount of "aging," Hanford rhodium can be used about 10 years earlier than Yankee.

TABLE IV

DOSE RATES FROM SOME FISSION PRODUCT RHODIUM SOURCES

		<u>Dose Rates, mR/hr.</u>			
<u>Cooling Time</u>		<u>Yankee</u>		<u>Hanford</u>	
		<u>1 ft.</u>	<u>1 M</u>	<u>1 ft.</u>	<u>1 M</u>
<u>Case I</u>	At discharge	4500	400	250	22
	10 y	160	15	11	1
	20 y	15	1	1	0.1
	30 y	1	0.1	0.1	0.01
<u>Case II</u>	At discharge	170	15	10	0.9
	10 y	15	1.4	0.9	0.08
	20 y	1	0.1	0.08	0.007
	30 y	0.1	0.01	0.008	0.0003
<u>Case III</u>	At discharge	8200	1401	450	77
	10 y	300	51	20	3
	20 y	27	5	2	0.3
	30 y	2.5	0.4	0.2	0.03

CONCLUSIONS

The radioactivity associated with fission product rhodium should not restrict its use in cases where small sources are required such as in electrical contacts or small dies, but for large sources such as catalyst beds the restrictions will be severe if power-reactor-produced rhodium with short cooling times is used. Even rhodium produced in the Hanford production reactors will require special handling procedures for several years after reactor discharges. The obvious conclusion to be reached is that the rhodium should be held in storage for an extended period of time, perhaps 15-30 years, before it is injected into commercial channels. One possible way to approach this problem is to develop a process which will isolate the rhodium from most of the radioactive waste in the fuels reprocessing plant, and store it separately. When the required aging period has elapsed, the rhodium can be further purified and placed in use. To be practical, such an isolation process must add very little cost to the fuel reprocessing operation, and the storage costs must be held to a minimum.

Unlike rhodium, the fission product palladium does not improve significantly with age as its radioactive component has a half life of 7×10^6 years. It does not have a dose rate hazard associated with its use but will be restricted because of the MPC limits. These MPC values have been recently reviewed.⁽⁸⁾ The 40-hour limiting occupational MPC values for soluble ^{107}Pd are 3×10^{-3} and 2×10^{-6} $\mu\text{Ci/cc}$ for air and water, respectively. For insoluble ^{107}Pd the values are 4×10^{-2} and 5×10^{-6} $\mu\text{Ci/cc}$. The specific activity is about 100 $\mu\text{Ci/g}$, so to convert to a weight basis the values are divided by 100. For example, the MPC for insoluble palladium in water is 4×10^{-4} g/cc. For a great many industrial uses these limits will present no problems.

FUTURE WORK

The work done to date on this study has pointed up some areas requiring further study. A lack of good data on the half-life of ^{102m}Rh and the cross section for the neutron reactions producing both ^{102}Rh and ^{102m}Rh prevent accurate predictions of the quality of fission product rhodium. Also more experimental data is needed to find the relation between rhodium quality and reactor exposure.

In the coming year we will begin a measurement of ^{102m}Rh half-life using the well-aged and highly purified rhodium from the Hanford reactor. This material is ideally suited for this measurement because it contains an extremely small amount of ^{102}Rh . The absence of ^{102}Rh will permit an accurate determination in a shorter time than "green" rhodium.

Determination of the cross section for the reaction $^{103}\text{Rh} \xrightarrow{(n, 2m)}$ ^{102m}Rh will be made by irradiating natural rhodium under controlled conditions and measuring the amount of ^{102}Rh and ^{102m}Rh which is formed.

Also, several more samples of rhodium will be recovered from the Yankee sub-assembly at positions to give a wide range of exposures. If fuel from another reactor type can be obtained, it will also be evaluated.

Further work on palladium will include the measurement of its isotopic composition by mass spectrographic techniques.

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FIGURE 1
Gamma Spectra of Fission Product Rhodium

FIGURE 2
Dose Rates from Pt-Rh Catalyst Bed