Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

(2 D)

AEC Research and Development Report

THE RADIATION CHARACTERISTICS OF
REACTOR PRODUCED RHODIUM,
PALLADIUM, RUTHENIUM AND
TECHNETIUM

OCTOBER 1972

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately-owned rights.

PACIFIC NORTHWEST LABORATORY

operated by

BATTELLE

for the

U.S. ATOMIC ENERGY COMMISSION

Under Contract AT(45-1)-1830

Printed in the United States of America

Available from

National Technical Information Service

U.S. Department of Commerce

5285 Port Royal Road

Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.95

3 3679 00062 1500

BNWL-1693
UC-4
Chemistry

THE RADIATION CHARACTERISTICS OF REACTOR
PRODUCED RHODIUM, PALLADIUM,
RUTHENIUM AND TECHNETIUM

by

F. P. Roberts
Chemical Technology

October 1972

BATTELLE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

THE RADIATION CHARACTERISTICS OF REACTOR
PRODUCED RHODIUM, PALLADIUM,
RUTHENIUM AND TECHNETIUM

by

F. P. Roberts

ABSTRACT

The radiation characteristics of reactor produced rhodium, palladium, ruthenium and technetium are reviewed for their potential utilization as substitutes or supplements for conventional resources.

The isotopic compositions of rhodium and palladium produced in a typical light-water reactor were experimentally determined. The half-life of ^{102m}Rh was measured and a value of 3.4 years was obtained. Measured dose rates of the fission products palladium and technetium were obtained, and dose rates for rhodium were calculated.

Examination of the radiological hazards associated with these fission products indicates that utilization is possible, but that restrictions must be applied to prevent injury to workers, dispersion of radioactivity to the environment and contamination of the world's stock of nonradioactive materials.

CONTENTS

ABSTRACT	iii
LIST OF FIGURES.	v
LIST OF TABLES	v
INTRODUCTION	1
EXPERIMENTAL.	1
RADIATION CHARACTERISTICS OF RHODIUM	3
Concentration of ^{102}Rh and $^{102\text{m}}\text{Rh}$ in Fission Product Rhodium.	3
Half-Lives of $^{102\text{m}}\text{Rh}$ and ^{102}Rh	4
Decay of $^{102\text{m}}\text{Rh}$ and ^{102}Rh	6
Dose Rates from Fission Product Rhodium.	6
RADIATION CHARACTERISTICS OF PALLADIUM	11
Isotopic Composition of Palladium	11
Dose Rate Measurement of Palladium	13
RADIATION CHARACTERISTICS OF RUTHENIUM	14
Composition of Fission Product Ruthenium	14
Decay of ^{106}Ru	15
Heat Generation from the Decay of Fission Product Ruthenium	17
RADIATION CHARACTERISTICS OF TECHNETIUM.	17
RADIOLOGICAL ASPECTS RELATED TO THE USE OF RHODIUM, PALLADIUM, RUTHENIUM AND TECHNETIUM	18
External Radiation.	18
Internal Radiation	21
Release of Radioactivity to Environment	22
REFERENCES	25

LIST OF FIGURES

1	Effect of Uncertainty of Half-Life of Estimated Specific Activity of ^{102m}Rh	5
2	Simplified Decay Scheme for ^{102m}Rh and ^{102}Rh	7
3	Gamma Spectra of Fission Product Rhodium	8
4	Dose Rate from a Hypothetical Catalyst Bed as a Function of Rhodium Cooling Time	10
5	Decay Scheme of ^{106}Ru - ^{106}Rh	16
6	Specific Activity of Rh and Ru Isotopes as a Function of Decay Time	20

LIST OF TABLES

1	Composition of Fission Product Rhodium	4
2	Gamma Ray Energies and Yields of ^{102}Rh and ^{102m}Rh	7
3	Calculated Dose Rates from Fission Product Rhodium Sources	9
4	Isotopic Composition of Fission Product Palladium	12
5	Estimated ^{106}Ru Activity in Ruthenium from Various Reactors.	15
6	Principal Gamma Energies and Yields from Decay of ^{106}Rh	16
7	Radiation Characteristics of Rh, Pd, Ru and Tc Isotopes	19
8	Internal Dose from Fission-Produced Palladium	21
9	Limiting Occupational MPC Values for ^{102}Rh , ^{102m}Rh and ^{107}Pd ($\mu\text{Ci}/\text{cm}^3$)	23
10	Cumulative Air Concentrations of Fission Product Palladium	24

THE RADIATION CHARACTERISTICS OF REACTOR
PRODUCED RHODIUM, PALLADIUM,
RUTHENIUM AND TECHNETIUM

by

F. P. Roberts

INTRODUCTION

Rhodium, palladium, ruthenium and technetium are produced in practical amounts as by-products of the nuclear power industry. These by-products are of interest because of their potential as supplements or substitutes for "natural" source raw materials. Unlike strontium, cesium, promethium, etc., which can be exploited because of their radioactive properties, the utilization of the platinum metals and technetium may be realized in spite of their radioactivity.

A knowledge of the radiation characteristics of these elements is essential for the evaluation of their potential uses. This report presents data describing amount and nature of the radiation associated with these by-products and discusses some of the aspects of the radiological hazards associated with their commercial use.

EXPERIMENTAL

The power reactor produced rhodium and palladium which were used for these experimental measurements were separated from a spent fuel sub-assembly from the Yankee Reactor. The subassembly consisting of UO_2 clad in stainless steel had an average burnup of 35,000 MWd/t and was discharged in August 1965. The rhodium and palladium from this fuel are reasonably typical of what can be expected from light-water reactors of the 1970 or 1980 designs.⁽¹⁾

The well-aged rhodium used in the half-life measurement was recovered from stored Hanford wastes^(2,3) and was made available to us by Atlantic Richfield Hanford Company. The palladium used for the dose rate measurement also came from this source.

Three samples of the Yankee subassembly were processed to recover the rhodium and palladium. The very high level of radioactivity made it necessary to perform the isolation and initial purification steps in a hot cell. The rods were cut into 1 in. sections and were treated with 8.0M nitric acid to dissolve the fuel. After evaporation to near dryness to remove most of the nitric acid and dilution with water, the solution was saturated with hydrogen sulfide. The precipitate which was formed contained the rhodium and palladium, but it was highly contaminated with ruthenium, silver, antimony and tellurium and probably technetium. The bulk of the ruthenium was removed by adding sulfuric and perchloric acids and by heating to distill off the ruthenium. Hydrobromic acid was then added and the solution was again heated to distill off antimony. Finally the rhodium and palladium were precipitated from the sulfuric acid solution by addition of hydriodic acid. At this point sufficient decontamination had been achieved to permit removal from the hot cell.

A final purification was carried out to remove the residual ^{110m}Ag , ^{125}Sb , ^{106}Ru , ^{137}Cs , ^{134}Cs , as well as minor amounts of other radioactivities. The ruthenium and antimony distillation steps were repeated using inert carriers. This was followed by conversion of the rhodium and palladium to soluble nitrites and by performing a series of ferric hydroxide scavenges using hold-back carriers of silver and cesium. The rhodium was precipitated as potassium rhodonitrite and the palladium as palladium dimethylglyoximate.

The rhodium and palladium mixture obtained from Atlantic Richfield Hanford Company was slightly contaminated and it was therefore, carried through the final purification steps described in the previous paragraph.

RADIATION CHARACTERISTICS OF RHODIUM

The principal isotope of rhodium which is formed in power reactors is stable ^{103}Rh . Unfortunately, from the standpoint of utilization, ^{102}Rh and $^{102\text{m}}\text{Rh}$ are also produced by the secondary reaction:

The two isomers of ^{102}Rh are radioactive and although they are produced in very low abundance, their presence represents a health hazard in most applications for which the use of fission product rhodium can be projected. It is the radiation characteristics of these rhodium activities that are of concern in this study. Their concentration, half-lives, decay schemes, associated dose rates and permissible concentrations in the environment are pertinent in assessing the feasible utilization of rhodium produced in power reactors.

CONCENTRATION OF ^{102}Rh AND $^{102\text{m}}\text{Rh}$ IN FISSION PRODUCT RHODIUM

The isotopic composition of rhodium produced in power reactors was determined experimentally by gamma energy analyses of the highly purified rhodium separated from the spent Yankee fuel. Three samples containing measured amounts of rhodium in aqueous solution were counted using a high resolution Ge(Li) detector and a multichannel pulse height analyzer. The specific activities were calculated from these measurements using the accepted decay schemes.

In addition to the measurements on the rhodium from the Yankee fuel, analysis of a sample of rhodium separated from 12-year-old high-level waste from Hanford was carried out.

The measured values obtained at the time of measurement for the $^{102\text{m}}\text{Rh}$ and ^{102}Rh content of these samples and the values corrected for decay back to the date of reactor discharge are given in Table 1.

TABLE 1. Composition of Fission Product Rhodium

Source	Burnup MWd/T	Isotopic Composition, $\mu\text{Ci/g Rh}$			
		Measured Values		Corrected for Decay to Discharge Date	
		^{102}Rh	$^{102\text{m}}\text{Rh}$	^{102}Rh	$^{102\text{m}}\text{Rh}$
Yankee	33,000	25 ± 10	120 ± 25	1900 ± 700	280 ± 60
Yankee	33,000	25 ± 10	130 ± 25	1900 ± 700	300 ± 60
Yankee	27,000	35 ± 10	180 ± 40	2600 ± 1000	420 ± 90
Hanford 13-yr-old	not detectable		1.7 ± 0.5	---	20 ± 6

The isotopic composition of the rhodium from the Yankee reactor is an acceptable basis for estimating the $^{102\text{m}}\text{Rh}$ and ^{102}Rh levels for light-water reactors of current design. Because of the unknown variables which can affect the generation of these undesirable isotopes, the values obtained here should not be used for projecting the composition of rhodium in future reactor design concepts such as the LMFBF (Liquid Metal Fast Breeder Reactor) and the HTGR (High Temperature Gas-Cooled Reactor).

A careful search was made to determine if any gamma emitting isotopes of rhodium other than $^{102\text{m}}\text{Rh}$ or ^{102}Rh were present in the Yankee samples. No evidence was found to indicate the presence of photopeaks except for those attributed to $^{102\text{m}}\text{Rh}$ or ^{102}Rh , and if others are present they exist in insignificant amounts.

HALF-LIVES OF $^{102\text{m}}\text{Rh}$ AND ^{102}Rh

The half-life of $^{102\text{m}}\text{Rh}$ has been reported to be 2.9 years^(4,5) and that of ^{102}Rh to be 206 days.⁽⁶⁾ The accuracy of the values of the longer lived $^{102\text{m}}\text{Rh}$ is of considerable importance in the estimation of residual radioactivity of fission product rhodium after a given storage time. The use of an incorrect value for projecting the future specific activity of ^{102}Rh can result in a significant error. The magnitude of the error is

graphically illustrated in Figure 1. It shows the calculated specific activities as a function of time since reactor discharge, using various assumed values for the half-life of ^{102}Rh in rhodium recovered from a fuel typified by the Yankee fuel.

FIGURE 1. Effect of Uncertainty of Half-Life of Estimated Specific Activity of ^{102m}Rh

The value of the half-life of ^{102m}Rh was measured at this laboratory by following the decay of three specimens of very well-aged rhodium recovered from the stored Hanford waste. The rhodium was 13 years old at the beginning of the measurement and therefore, it was assumed to contain insignificant amounts of the 206 day old ^{102}Rh . This is assumed because the ^{102}Rh had decayed for 23 half-lives and therefore, retained only $1.1 \times 10^{-5}\%$ of its initial activity.

The rhodium used for the half-life measurement was painstakingly purified to remove all traces of radioactive impurities, and then it was sealed in 3 glass containers to prevent evaporation. Each contained 20 to 40 mg rhodium (0.04 to 0.08 $\mu\text{Ci } ^{102\text{m}}\text{Rh}$) in 10 ml hydrochloric acid solution.

The samples were counted twice per week over a 115 week period using a gamma energy analyzer system with a high resolution Ge(Li) diode detector. The counting time was selected to give a minimum of 10^4 counts in the 0.475 MeV photopeak.

The counting data was treated by regression analysis to obtain the measured half-life and the confidence limits. Independent values were obtained using data from two major photopeaks (0.475 MeV and 0.675 MeV). The most probable value for the half-life is 3.40 ± 0.25 years.

DECAY OF $^{102\text{m}}\text{Rh}$ AND ^{102}Rh

$^{102\text{m}}\text{Rh}$ decays by the electron capture process. ^{102}Rh also decays predominantly by electron capture but in addition, 3.4% goes by positron emission and 16% by beta emission. The electron capture and positron decay give rise to excited levels of ^{102}Ru which de-excite by emission of gamma rays. The beta decay of ^{102}Rh goes directly to the ground state of ^{102}Pd and produces no gammas. A simplified decay scheme is shown in Figure 2. The gamma energies and yields are given in Table 2. The gamma spectra of specimens containing only $^{102\text{m}}\text{Rh}$ from well-aged rhodium and a mixture of $^{102\text{m}}\text{Rh}$ and ^{102}Rh from short cooled rhodium are shown in Figure 3.

DOSE RATES FROM FISSION PRODUCT RHODIUM

Massive amounts of fission product rhodium will produce significant radiation dose rates due to the presence of $^{102\text{m}}\text{Rh}$ and ^{102}Rh . Actual dose rates were not measured experimentally because the available amount of rhodium from power reactors was insufficient to give meaningful information. However, calculations were performed to show the magnitude of the dose rate which will be encountered in the utilization of rhodium.

FIGURE 2. Simplified Decay Scheme for $^{102\text{m}}\text{Rh}$ and ^{102}Rh

TABLE 2. Gamma Ray Energies and Yields of ^{102}Rh and $^{102\text{m}}\text{Rh}$ (6)

Energy, KeV	Yield, Number of Gammas Per Decay	
	^{102}Rh (206 day half-life)	$^{102\text{m}}\text{Rh}$ (3.4 year half-life)
418.5	None	0.13
475.2	0.57	0.95
511.0(a)	0.25	None
632.0	0.04	0.54
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

a. The 511 KeV gamma is from positron annihilation.

FIGURE 3. Gamma Spectra of Fission Product Rhodium

Estimated dose rates were obtained by computer calculations using the QAD program developed by Malenfort.⁽⁷⁾

- Case I. The source consisted of a right circular cylinder with equal height and diameter containing 81 cm^3 rhodium with a density of 12.4 g/cm^3 and a weight of 1 kg.
- Case II. The source consisted of 1 kg 90% platinum - 10% rhodium alloy, but otherwise identical to Case I.
- Case III. The source consisted of a catalyst bed for a 300 ton/day nitric acid plant. The catalyst bed was fabricated of layers of 80 mesh weave in the shape of a hexagon 54 in. on the diagonal. The total weight was 20 kg of 90% platinum - 10% rhodium alloy.

The isotopic compositions of the rhodium used for these hypothetical sources were the average values obtained from the measurements on the rhodium recovered from the 33,000 MWd/t Yankee reactor fuel. The values used were 1900 $\mu\text{Ci/g}$ for ^{102}Rh and 290 $\mu\text{Ci/g}$ for ^{102m}Rh at the time of reactor discharge.

The dose rates were calculated for distances of 1 ft and 1 m from the source for each of the above cases, and the results are given in Table 3.

TABLE 3. Calculated Dose Rates from Fission Product Rhodium Sources^(a)

	<u>Cooling Time, yr</u>	<u>Dose Rate, mR/hr</u>	
		<u>at 1 ft</u>	<u>at 1 m</u>
Case I	at discharge	4500	400
	10	240	23
	20	32	3
	30	3	0.13
Case II	at discharge	170	15
	10	23	2.1
	20	2.2	0.2
	30	0.3	0.03
Case III	at discharge	8200	1401
	10	460	78
	20	58	11
	30	7.8	1.2

a. Based on use of rhodium from Yankee reactor fuel of 33,000 MWd/t exposure.

The dose rates from massive sources of short-cooled fission product rhodium are, indeed, large; but as the cooling time increases, they become increasingly more tolerable as shown in Figure 4. For example, the practical case of a catalyst bed for a nitric acid plant gives a dose rate

of only 240 mR/hr at 1 m using 5-year-old rhodium. This level of radioactivity would, of course, require special handling and under controlled conditions safe utilization of rhodium is conceivable.

FIGURE 4. Dose Rate from a Hypothetical Catalyst Bed as a Function of Rhodium Cooling Time

RADIATION CHARACTERISTICS OF PALLADIUM

Palladium as produced in nuclear reactors in significant amounts is a mixture of the following isotopes: ^{104}Pd , ^{105}Pd , ^{106}Pd , ^{107}Pd , ^{108}Pd , ^{109}Pd and ^{110}Pd . Of these only ^{107}Pd is radioactive. Minor amounts of other radioactive isotopes are formed, but none of these are known to have half-lives of more than a few hours; they will have decayed to immeasurably low levels prior to the reprocessing of the reactor fuel.

^{107}Pd decays to stable ^{107}Ag by beta emission with a half-life of 7×10^6 . The maximum beta energy is 0.04 MeV.⁽⁸⁾ Two obvious but important conclusions can be drawn from these facts:

- Because of the very long half-life of ^{107}Pd , the passage of time will not reduce the radioactivity of fission product palladium for all practical purposes.
- Because of the low energy beta and lack of any gamma emission associated with the decay of ^{107}Pd , the utilization of fission product palladium requires little shielding to protect the user against the radiation dose.

The only experimental work carried out was the determination of the isotopic composition of power reactor produced palladium, and the measurement of its radiation dose rate. The purpose of the experiments was to verify and to demonstrate the relatively low magnitude of radiation hazards from the handling and use of fission product palladium.

ISOTOPIC COMPOSITION OF PALLADIUM

Measurement of the ^{107}Pd content (the only known radioactive component of fission product palladium) could not easily be accomplished by counting methods because of the very low energy of the beta emitted in the decay. Instead, mass spectrographic analysis was used to determine the principal isotopes, and gamma energy analysis was used to search for unknown gamma emitting isotopes.

Two samples of approximately 50 mg of palladium separated from the Yankee fuel served for the mass spectrographic measurements. Great care was taken to separate all nonpalladium elements from the samples, particularly elements such as rhodium, ruthenium, and silver which have isotopes of the same masses as the expected palladium masses (mass 104 to 110). Emission spectrographic analysis of the purified sample indicated that satisfactory purity was achieved. The mass spectrographic analyses of the two samples are given in Table 4.

TABLE 4. Isotopic Composition of Fission Product Palladium

<u>Isotope Mass No.</u>	<u>wt% of Isotope</u>	
	<u>Sample 1</u>	<u>Sample 2</u>
104	14.3	14.3
105	22.0	21.9
106 ^(a)	33.2	32.7
107	16.8	17.0
108	10.9	11.3
110	3.8	2.8

a. ^{106}Pd grows in the unseparated fission product mixture from the decay of ^{106}Ru .

The separation was carried out 3.5 years after reactor discharge and >90% of the ^{106}Ru had decayed to ^{106}Pd at that date. Using the average value of 16.9 wt% for ^{107}Pd from the two analyses, the specific activity for ^{107}Pd based on the accepted half-life of 7×10^7 years is 8.1 $\mu\text{Ci/g}$ of palladium.

The search for unknown gamma emitting isotopes or isomers of palladium was accomplished by gamma energy analysis of a radiochemically pure sample of the palladium from the Yankee fuel. The experimental method used was one of repetitive purification steps followed by measurement of residual

gamma activity. The purification counting cycle was continued until the level of radioactivity reached the limit of detection of the gamma counting system, i.e., the background level. Each purification consisted of three steps:

1. Fuming with sulfuric-perchloric acids to volatilize ruthenium
2. Precipitation of palladium iodide
3. Precipitation of palladium dimethylglyoximate.

These steps were carried out in the presence of hold-back carriers of cobalt, ruthenium, silver, cesium, and antimony which were the most persistent impurities. Four purification cycles were required to achieve the desired purity. After the last cycle, 22 mg of palladium remained of the original 100 mg starting material.

The gamma counter used was 3 in. x 3 in. NaI (Tl) crystal and a 400 channel pulse-height analyzer. The efficiency of the counting system was known, and it was possible to estimate the approximate limit of detection.

From an evaluation of the gamma counting data, it was concluded that if gamma emitting isotopes of palladium exist, they are present at a level less than 0.02 $\mu\text{Ci/g}$ palladium.

DOSE RATE MEASUREMENT OF PALLADIUM

The dose rate from reactor produced palladium was experimentally measured to verify that the ^{107}Pd will present no serious dose problems to users.

There was not a large enough quantity of fission product palladium available at the time of the measurement to provide a massive source, but a suitable source was simulated by plating the available fission product palladium on a sheet of nickel metal. The range of ^{107}Pd beta is about 4 mg/cm², and a palladium plate of this thickness should present the same beta dose rate as an infinitely thick slab of palladium.

The source used for the dose rate measurement was prepared by electrodepositing 0.5 g of fission product palladium on an 8 cm x 8 cm sheet of nickel. The thickness of the plate was 8 mg/cm^2 or about twice the range of the ^{107}Pd beta.

The dose rate was measured by means of an extrapolation chamber both with and without a 7 mg/cm^2 absorber. The observed surface dose rate was 0.8 r/hr unshielded and zero through the 7 mg/cm^2 absorber.

This measurement shows that the dose rate from fission product palladium results principally from the low energy beta and that this dose is reduced to a negligible level by a very thin shield. The 7 mg/cm^2 shield used in the measurement is equivalent to the human skin, and it can be concluded that biological damage, if any, due to external sources of palladium will be confined to the skin surface.

RADIATION CHARACTERISTICS OF RUTHENIUM

Ruthenium, unlike rhodium and palladium, is extremely radioactive at the time of reactor discharge. The radioactivity is from the decay of ^{103}Ru and ^{106}Ru . There are no other ruthenium isotopes likely to be formed which have half-lives greater than a few hours. ^{103}Ru has a half-life of 39.5 days and ^{106}Ru has a half-life of 368 days. (9)

The controlling radioactivity is due to ^{106}Ru , and although it is present in huge amounts initially, its decay rate is rapid enough so that eventual utilization is not ruled out. However, fission product ruthenium can be considered to be a usable resource only after long term storage.

COMPOSITION OF FISSION PRODUCT RUTHENIUM

Reactor produced ruthenium contains the stable isotopes ^{99}Ru , ^{100}Ru , ^{101}Ru , ^{102}Ru and ^{104}Ru as well as the radioactive isotopes ^{103}Ru and ^{106}Ru . The ^{103}Ru (39.6 days) is not of concern since it has a relatively

short half-life and it will have decayed to a minor fraction of the total ruthenium radioactivity by the time the fuel is reprocessed. The ^{106}Ru activity, on the other hand, is very large and is the controlling factor in ruthenium utilization.

The specific activity of ^{106}Ru in ruthenium from power reactors will vary somewhat depending on the reactor type. Estimates of ruthenium composition produced in BWR's (Boiling Water Reactor's) and PWR's (Pressurized Water Reactor's) of 1970 and 1980 designs taken from Deonigi's data⁽¹⁾ are shown in Table 5. The values range from 216 to 271 Ci/g of stable ruthenium, and an average value of ~ 245 Ci/g is sufficiently accurate for evaluation purposes.

TABLE 5. Estimated ^{106}Ru Activity in Ruthenium from Various Reactors

Reactor Type	Stable Ru g/MT	^{106}Ru g/MT	Specific Activity of ^{106}Ru Ci/g of Stable Ru
Boiling Water 1970 Design	1702	116	228
Boiling Water 1980 Design	1487	114	257
Pressurized Water 1970 Design	1842	119	216
Pressurized Water 1980 Design	1410	119	271

DECAY OF ^{106}Ru

When considering the radiation characteristics of fission product ruthenium, it is necessary to take into account both the decay of the ^{106}Ru and its short-lived daughter ^{106}Rh . The daughter has a half-life of 30 sec and for practical purposes is always in equilibrium with the parent. The parent ^{106}Ru decays by beta emission to ^{106}Rh . The maximum energy of the beta is 0.0392 MeV⁽⁸⁾ and there is no gamma. The decay of ^{106}Rh is by beta emission to ^{106}Pd . Approximately 80% of the decays go directly to the ground state of ^{106}Pd , but the remainder go to excited

states which decay to the ground state with the emission of gammas. A simplified decay scheme is shown in Figure 5. The principal gamma energies and yields are given in Table 6.

FIGURE 5. Decay Scheme of ^{106}Ru - ^{106}Rh (8)

TABLE 6. Principal Gamma Energies and Yields from Decay of ^{106}Rh

<u>Energy, MeV</u>	<u>Yield, %</u>
0.512	21
0.622	11
1.05	1.5
1.13	0.5
1.55	0.2

HEAT GENERATION FROM THE DECAY OF FISSION PRODUCT RUTHENIUM

The amount of heat generation from the decay of ^{106}Ru and its daughter ^{106}Rh will be a factor in the design of recovery and storage facilities used for ruthenium recovery. The heat generation has been calculated from the decay energies. The total rate is 9.76 W/kCi of ^{106}Ru . This rate includes the energy released from the decay of both parent and daughter. Of this, 9.7 W comes from the daughter. Based on the ^{106}Ru content at reactor discharge as given in Table 5, the rate is 2.1 to 2.6 kW/kg of stable ruthenium.

RADIATION CHARACTERISTICS OF TECHNETIUM

The only known technetium isotope expected to be found in reactor fuels at the time of processing is ^{99}Tc . ^{99}Tc is a pure beta emitter with a half-life of 2.12×10^5 years.⁽¹⁰⁾ The maximum energy of the beta particle is 0.292 MeV.⁽¹¹⁾ The specific activity is 16.98 mCi/g. It is likely that small amounts of ^{98}Tc are formed by a (n,2n) reaction with ^{99}Tc . The activity due to ^{98}Tc would be very small because of the relatively small cross-section for the (n,2n) reaction and the very long half-life of ^{98}Tc (1.5×10^6 years). ^{98}Tc decays with emission of energetic gammas. This emission would be easily detectable but no evidence for its presence has been reported. All other known isotopes of technetium which could be found have half-lives of no more than a few hours, and they will have decayed to negligible levels by the time the spent fuels are processed.

No experimental work was carried out in this study to evaluate the radiation characteristics of technetium. In previous work the surface dose rate from a source of technetium was measured.⁽¹²⁾ The measurement was made using a piece of pure technetium metal 0.037 in. thick which is essentially infinite for the 0.292 MeV ^{99}Tc beta. The measured surface dose was 1250 rad/hr. Almost the entire dose rate was due to the beta emission.

The maximum range of the ^{99}Tc beta is less than 80 mg/cm^2 . Very little shielding is required to reduce its dose rate to a safe working level. At this laboratory, when working with quantities from a few grams to several hundred grams, the necessary shielding to the hands was provided by wearing two pairs of surgeons gloves.

RADIOLOGICAL ASPECTS RELATED TO THE USE OF RHODIUM, PALLADIUM, RUTHENIUM AND TECHNETIUM

The radiation characteristics of the isotopes of Rh, Pd, Ru and Tc discussed above are summarized in Table 7. Each of the elements has a radiologically significant amount of radioactivity associated with it, and any given application must be evaluated in terms of the radiological hazards inherent in the use of such materials.

The limiting activity in rhodium is the 3.4 year $^{102\text{m}}\text{Rh}$; 368 day ^{106}Ru is the limiting activity in ruthenium. Figure 6 shows graphically the decay of the radioactive components in rhodium and ruthenium. Palladium and technetium each have one radioactive component. In both cases the half-lives are very long, and therefore, they both have essentially constant specific activities.

The radiological factors which need to be considered in evaluating the potential use of any of these elements include the direct effects of radiation, the potential for dispersion in the environment and the possible contamination of "natural" source rhodium, palladium and ruthenium due to recycling and reuse.

EXTERNAL RADIATION

The direct effects of radiation stem from the dose rates from external sources or internal sources (resulting from ingestion or inhalation). Rhodium, ruthenium and technetium all give rise to significant external dose rates which require the use of special protective measures such as radiation

TABLE 7. Radiation Characteristics of Rh, Pd, Ru and Tc Isotopes

Isotope	Half-Life	Decay Mode	Maximum Beta Energy, MeV	Gamma Energies MeV	Specific Activity ⁽¹⁾ Microcuries/gram
^{102}Rh	206 days	Beta Positron E.C.	1.29	0.475 (57%) 0.511 (25%) 0.632 (54%) 0.698 (41%) 1.110 (22%)	1900
$^{102\text{m}}\text{Rh}$	3.4 yr	E.C.	None	0.418 (13%) 0.475 (95%) 0.632 (54%) 0.768 (30%) 1.050 (41%) 1.110 (22%)	290
^{107}Pd	7×10^6 yr	Beta	0.04	None	81
^{103}Ru	39.6 days	Beta	0.07	0.497 (88%) 0.610 (6%)	5×10^9
^{106}Ru	368 days	Beta	$3.54^{(2)}$	$0.512^{(2)}$ (21%) 0.622 (11%) 1.050 (1.5%) 1.130 (0.5%) 1.550 (0.2%)	5×10^8
^{99}Tc	2.12×10^5	Beta	0.292	None	1.7×10^4

1. The specific activities are for the fission product mixture at reactor discharge.

2. These include the daughter radiations from ^{106}Ru .

shields, remote manipulation, etc. Palladium, on the other hand, generates an insignificant external dose rate and the principal safeguard requirement is the prevention of ingestion or inhalation.

FIGURE 6. Specific Activity of Rh and Ru Isotopes as a Function of Decay Time

To place the magnitude of external dose rates in perspective, the example of the nitric acid plant catalyst bed is used. This bed containing 2 kg of fission product rhodium generates a dose rate of 420 mR/hr at 1 m assuming 2.5 year cooled rhodium. The problems attendant to the fabrication, handling, and plant-use of such a bed are severe and would undoubtedly require a highly restrictive license. This same catalyst bed fabricated of 20-year-old rhodium would generate a dose rate of only 11 mR/hr at 1 m, but even at this level special precautions would be required. Direct contact would be prohibited and some radiation shielding would be required to protect workers. Special techniques for fabrication and installation of the unit would have to be developed. The stringency of the radiation protection procedures are lessened the older the rhodium is, but many years of decay are required before unrestricted use can be contemplated.

Applications involving massive amounts of short-cooled ruthenium cannot be considered for ordinary industrial application because of the very high gamma dose rate due to the presence of ^{106}Ru . Because of the 1-year half-life, the activity decreases rapidly. The initial amount is very large and approximately 25 year decay is necessary to reduce the specific activity to $10\ \mu\text{Ci/g}$ which might be a reasonable level for some restricted uses. Unrestricted use may require a 35 to 50 year decay period.

Fission product palladium has about $80\ \mu\text{Ci}$ of $^{107}\text{Pd/g}$ of palladium. The ^{107}Pd emits a 0.035 MeV beta and no gamma. The range of the 0.035 MeV beta is about $4\ \text{mg/cm}^2$, almost identical to the ^{239}Pu alpha range. A typical palladium relay contact⁽¹³⁾ is about 0.051 cm wide by 0.025 in. thick and contains 0.79 mg of Pd. Only 1% of the ^{107}Pd betas will be emitted from the surface of this contact if it is made from fission product palladium. If this palladium contact is placed on the skin, the dose rate will be 1.6 rad/hr because all the ^{107}Pd beta energy will be absorbed in a volume element defined by the width of the contact and the range of the ^{107}Pd beta. Since all the energy is absorbed in the skin, the dose may not be biologically significant. The exact significance of this dose to the skin is yet to be defined.

INTERNAL RADIATION

Another set of calculations were made to show the internal hazard of radiopalladium. In this case, it was assumed that 10 g and 1000 g of insoluble Pd were ingested with no biological adsorption. Table 8 summarizes these calculations.

TABLE 8. Internal Dose from Fission-Produced Palladium

Organ	Mass, g	Avg Residence Time, hr	Dose, rad	
			10 g	1000 g
Stomach	250	0.042	0.036	3.6
Small Intestine	400	0.167	0.088	8.8
Upper Intestine	220	0.542	0.520	52.0
Lower Large Intestine	135	24.000	37.900	3790.0

Sullivan, et al.,⁽¹⁴⁾ have introduced millicurie amounts of insoluble Pu into the intestines of rats without detectable biological effect. The Pd dose rates are lower than those calculated for the Pu experiments and suggest that the biological effect of insoluble Pd should be less. These calculations suggest that fission-produced palladium may be used with a very minimal biological effect. Before this is done, experiments similar to those done by Sullivan, et al.⁽¹⁴⁾ should be done. The effect on lungs of inhalation of fission-produced palladium should also be determined.

Evaluation of the radiological hazards of technetium has not been made, but it is obvious that the high specific activity of ⁹⁹Tc will restrict general usage. Unlike palladium or well-aged rhodium and ruthenium, conventional applications for technetium cannot be foreseen. If cases develop in which the unique characteristics of technetium make its use desirable, the radiation involved must be taken into account. The radiation is by no means an impossible obstacle. At this laboratory we have worked with kilogram quantities of technetium preparing various chemical compounds, pure metal and alloys without serious incident. Only the normal precaution and specialized skills of a radiochemical laboratory were used to prevent exposure, contamination, or dispersion to the environment.

RELEASE OF RADIOACTIVITY TO ENVIRONMENT

The release of radioactivity to the environment as the result of the use of fission product rhodium, palladium, ruthenium and technetium is another potential problem which must be considered. The acceptable amounts of any radioactive substance in the air, water, or food supply are very small. For example, the limiting occupational MPC values for the rhodium and palladium isotopes as calculated by Soldat⁽¹⁵⁾ are given in Table 9. These MPC values should be divided by 20 to 30 for exposure to general members of the public.

Once again using the example of the catalyst bed for a nitric acid plant and the MPC values for rhodium, a "worst" case dispersion has been calculated. Assuming a catalyst bed containing 2 kg of 2 year cooled

TABLE 9. Limiting Occupational MPC Values for ^{102}Rh , $^{102\text{m}}\text{Rh}$ and ^{107}Pd ($\mu\text{Ci}/\text{cm}^3$)

Nuclide	Form	40 hr MPC ^(a)	
		Water	Air
^{102}Rh	Soluble	3×10^{-3}	4×10^{-7}
	Insoluble	2×10^{-3}	2×10^{-8}
$^{102\text{m}}\text{Rh}$	Soluble	2×10^{-3}	3×10^{-7}
	Insoluble	1×10^{-3}	1×10^{-8}
^{107}Pd	Soluble	3×10^{-2}	2×10^{-6}
	Insoluble	4×10^{-2}	5×10^{-7}
^{106}Ru	Soluble	4×10^{-4}	8×10^{-8}
	Insoluble	3×10^{-4}	6×10^{-9}
^{99}Tc	Soluble	1×10^{-2}	2×10^{-6}
	Insoluble	5×10^{-3}	6×10^{-8}

a. Values for rhodium and palladium isotopes taken from Reference 15. Values for ruthenium and technetium taken from Reference 16.

rhodium including $4 \times 10^5 \mu\text{Ci } ^{102}\text{Rh}$ and $4 \times 10^5 \mu\text{Ci } ^{102\text{m}}\text{Rh}$ is completely dispersed in the atmosphere, it would have to be diluted in only $2 \times 10^6 \text{ m}^3$ or $5 \times 10^{-4} \text{ mi}^3$ to attain the limiting air MPC. For the same case in which the catalyst is completely dispersed in an insoluble form in water, total volume of water would have to be 2×10^5 gallons or 0.61 acre feet to be within the stated MPC values for water. These extreme examples are intended to show the magnitude of the hazard which might be encountered. Even this "worst" case does not represent an event of catastrophic proportions.

For palladium the effect of similar incidents is much less severe because of the lower specific activity and higher MPC values. In another extreme calculation, it is assumed that all of the palladium produced in power reactors is dispersed as a finely divided material and that it is evenly distributed over the earth's surface up to a depth of 10 ft. The

cumulative concentrations of palladium under these conditions are shown in Table 10. The concentrations are much less than the MPC values even under these extremely unlikely conditions.

TABLE 10. Cumulative Air Concentrations of Fission Product Palladium

<u>Year</u>	<u>Grams</u>	<u>μCi</u>	<u>Pd Concentration $\mu\text{Ci}/\text{cm}^3$</u>
1975	2.86×10^6	2.8×10^8	2.2×10^{-13}
1980	1.26×10^7	1.0×10^9	1.0×10^{-12}
1985	3.50×10^8	2.8×10^{10}	2.6×10^{-12}
1990	7.71×10^8	6.2×10^{10}	5.8×10^{-12}

The high value of the platinum metals encourages recycle of recovered scrap and wastes. A large fraction of these metals are returned to the refineries for purification and then returned to the stream. Injection of the fission product metals into the stream could lead to contamination of the recycled platinum metals. This situation must be avoided to prevent the need for imposing restrictions on the use of all rhodium, palladium and ruthenium. This implies the need for segregation of the fission products from the "natural" source metals at all points in the utilization cycle.

In general, the radiological hazards from the reactor produced rhodium, palladium, ruthenium and technetium will necessitate controls and restrictions which will make their usage more costly than nonradioactive natural source metals. The radiological hazards do not prohibit the utilization of any of these fission products from a technical viewpoint, but economic constraints may prevent usage in the near term.

REFERENCES

1. D. E. Deonigi, R. W. McKee and D. R. Happner, Isotope Production and Availability from Power Reactors, AEC Research and Development Report, BNWL-716, 1968.
2. J. V. Panesko, Process for Purification of Fission Product Rhodium, Palladium and Technetium Recovered from Aged Purex Supernatant Wastes, AEC Research and Development Report, ARH-911, 1968.
3. J. V. Panesko, Process for Recovery of Rhodium, Palladium and Technetium from Aged Reprocessing Wastes at Hanford, AEC Research and Development Report, ARH-733, 1968.
4. P. Born, A. Veeffkind, W. H. Elsenaar and J. Blok, "An Isomeric State in ^{102}Rh ," Physica, vol. 29, pp. 535-536, 1963.
5. K. Hisatake, S. Matsuo and H. Kawakami, "Half-Life Measurements in Rh^{101} and $\text{Rh}^{102\text{m}}$," J. Phys. Soc., (Japan), vol. 20, p. 1107, 1965.
6. K. Hisatake, "Decay of Rh^{102} and Levels in Ru^{102} ," J. Phys. Soc., (Japan), vol. 16, p. 1280, 1961.
7. R. E. Malefant, QAD - A Series of Point Kernel General Shielding Programs, AEC Research and Development Report, LA-3573, 1967.
8. C. Michael Lederer, Jack M. Hollander and Isadore Perlman, Table of the Isotopes, 7th Ed., John Wiley and Sons, Inc., New York, 1967.
9. K. F. Flynn, L. E. Glendenin and E. P. Strinbers, "Half-Life Determinations by Direct Decay," Nucl. Sci. Eng., vol. 22, p. 416, 1965.
10. S. Fried, A. H. Jaffey, N. F. Hall and L. E. Glendenin, "Half-Life of the Long-Lived Tc^{99} ," Phys. Rev., vol. 81, p. 741, 1951.
11. S. L. Tatmoty, "The Beta-Spectrum of Tc^{99} ," Phys. Rev., vol. 81, p. 461, 1951.
12. R. G. Nelson and O. P. O'Keefe, Concluding Progress Report - A Study of Tungsten-Technetium Alloys, AEC Research and Development Report, BNWL-865, 1968.
13. Anon, "The Major Producers Get Set for the Future," Mining Eng., vol. 20, p. 73, 1968.
14. M. F. Sullivan, P. L. Hackett, L. A. George and R. C. Thompson, "Irradiation of the Intestine by Radioisotopes," Rad. Res., vol. 13, p. 343, 1960.
15. J. K. Soldat, "MPC Values for ^{102}Rh , $^{102\text{m}}\text{Rh}$, and ^{107}Pd ," Health Phys., vol. 19, p. 60, 1970.
16. Code of Federal Regulations 10CFR 20 10C-1, January 1, 1972.

DISTRIBUTIONNo. of
Copies
OFFSITE

1	<u>AEC Chicago Patent Group</u> G. H. Lee
195	<u>AEC Division of Technical Information Extension</u> UC-4
1	<u>AEC Division of Reactor Development and Technology</u> W. D. Holloman
2	<u>Oak Ridge National Laboratory (AEC)</u> J. H. Gillette A. F. Rupp
1	<u>AEC Patent Office</u>
1	<u>AEC Division of Research (Van Dyken)</u>
1	<u>AEC Library, Washington</u>

ONSITE

1	<u>AEC Chicago Patent Group</u> R. M. Poteat
2	<u>AEC Richland Operations Office</u> W. E. Lotz Attn: B. J. Melton H. A. House
8	<u>Atlantic Richfield Hanford Company</u> G. L. Borsheim H. H. Hopkins G. A. Nicholson G. C. Oberg A. E. Smith P. W. Smith M. J. Szulinski ARHCO Files

No. of
Copies

3 Donald W. Douglas Laboratories

M. Lewis
W. E. Matheson
Files

1 Douglas United Nuclear

J. W. Riches

58 Battelle-Northwest

E. M. Alpen
J. M. Batch
T. D. Chikalla
F. T. Cross
G. J. Dau
D. C. Deonigi
K. Drumheller
P. L. Farnsworth
J. W. Finnigan
H. T. Fullam
J. E. Hansen
A. J. Haverfield
J. H. Jarrett (4)
R. S. Kemper
L. L. Lahart
R. W. McKee
E. T. Merrill
J. E. Minor
J. M. Nielsen
R. E. Nightingale
R. W. Perkins
A. M. Platt
F. P. Roberts (20)
C. A. Rohrman
J. R. Sletager
K. L. Swinth
H. H. Van Tuyl
J. B. Vetrano
E. J. Wheelwright
N. A. Wogman
Technical Information Files (5)
Technical Publications