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**Recovery of Nonradioactive Palladium  
and Rhodium from High-Level  
Radioactive Wastes**

H. F. McDuffie

OAK RIDGE NATIONAL LABORATORY  
OPERATED BY OROSCOPE CORPORATION FOR THE DEPARTMENT OF ENERGY

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CHEMISTRY DIVISION

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FROM HIGH-LEVEL RADIOACTIVE WASTES

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## CONTENTS

|   | <u>Page</u> |
|---|-------------|
| ACKNOWLEDGMENTS . . . . .   | v           |
| ABSTRACT . . . . .  | 1           |
| 1. INTRODUCTION . . . . .   | 1           |
| 2. SOLUBILITY IN LIQUID METALS . . . . .  | 6           |
| 3. INTERMETALLIC COMPOUNDS, MUTUAL SOLUBILITY, AND<br>COPRECIPITATION . . . . . | 9           |
| 3.1 Equilibrium Precipitation . . . . .   | 9           |
| 3.2 Nonequilibrium Precipitation . . . . .                                      | 10          |
| 4. LIQUID-LIQUID EXTRACTION . . . . .   | 13          |
| 5. RECOVERY OF NONRADIOACTIVE RHODIUM . . . . .                                 | 16          |
| REFERENCES . . . . .  | 18          |

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## ABSTRACT

A possible method for recovering significant quantities of nonradioactive palladium from fission-product wastes requires essentially complete separation of the fission-product (radioactive) palladium from fission-product ruthenium. After the decay of  $^{106}\text{Ru}$  via  $^{106}\text{Rh}$  to  $^{106}\text{Pd}$ , this nonradioactive palladium is recovered for normal commercial use. The U.S. production of palladium has never been above 1000 kg per year vs consumption of about 46,000 kg per year. Most of the supply comes from Russia and South Africa. It has been estimated that a 400-GW(e) nuclear reactor economy will make available 2000 kg per year of  $^{106}\text{Ru}$  at reactor fuel discharge. A substantial increase might be achieved if plutonium were recycled as fissionable material because of the higher yields of the 106 chain from plutonium. A literature search has uncovered support for three promising approaches to the required separation of palladium from ruthenium: (1) recrystallization from solution in bismuth or in zinc; (2) selective precipitation of a titanium-ruthenium intermetallic compound from bismuth, followed by precipitation of a zinc-palladium intermetallic compound; and (3) dissolution in molten magnesium followed by partitioning between molten magnesium and a molten uranium-5 wt % chromium eutectic at a temperature above  $870^\circ\text{C}$ . Liquid-liquid extraction appears to be the most promising method from a technological point of view, although intermetallic compound formation is much more interesting chemically. Recovery of some nonradioactive  $^{103}\text{Rh}$  may be possible by liquid-liquid extraction of the fuel before the decay of the 39.8-d  $^{103}\text{Ru}$  has gone substantially to completion. Demonstration of the practicality of these separations will contribute a positive factor to the evaluation of resumption in the United States of nuclear fuel reprocessing and plutonium recycle in light-water-moderated reactors.

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### 1. INTRODUCTION

Most attempts to recover valuable products from irradiated nuclear reactor fuels have dealt with the recovery and use of radioactive isotopes, and there is a voluminous literature on this subject. A January 1978 report by Exxon Nuclear Company, Inc.<sup>1</sup> illustrates the currently unfavorable financial prospects for profitable separation and recovery of selected radioisotopes from commercial nuclear fuel wastes because of the U.S. government's position against reprocessing and the regulatory and safeguards problems.

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Battelle Northwest Laboratories (BNWL) reported the results of a 1972 market survey of the possibility of separating and recovering radioactive mixtures of the platinum-group metals which occur as fission products.<sup>2,3</sup> The BNWL study did not produce a strong case for economic separation and recovery, even at a time when reprocessing, regulatory, and safeguards costs were lower.

Reexamination of the possibilities for beneficial recovery of fission-product materials at the Oak Ridge National Laboratory (ORNL) has revealed a fortuitous combination of nuclear and chemical properties that makes it possible to visualize methods for recovering appreciable quantities of nonradioactive palladium from fission-product residues. The method is based on the premise that a complete removal of fission-product palladium from ruthenium, followed by a waiting period for the decay of 368-d  $^{106}\text{Ru}$  and its 30-s  $^{106}\text{Rh}$  daughter, produces nonradioactive  $^{106}\text{Pd}$ . Chemical separation of this palladium from the remaining  $^{106}\text{Ru}$  gives a product suitable for unrestricted commercial use.

The United States has never been a large producer of palladium. In 1966 it reached a high of 901 kg; in 1973, 404 kg; in 1974, 279 kg; and, with the cessation of placer mining in Alaska in 1976, the only remaining U.S. sources for platinum-group metals as a whole are by-products of copper refining. Consumption of palladium has been much greater than the amount produced: in 1974, 46,587 kg was used; there were increased demands in the automotive and dental industries. The greatest amount of palladium used in the United States comes from the Soviet Union; lesser amounts come from the Republic of South Africa. Thus the United States is in an economically and strategically uncomfortable position with respect to palladium (and other platinum metals), even though there is a substantial stockpile.

G. P. Dix<sup>4</sup> estimates that, in 1990, 2000 kg of  $^{106}\text{Ru}$  will be available from spent nuclear fuel. This estimate is based on an installed nuclear generating capacity of 400 GW(e), which considers only U.S. civilian reactors and light-water reactors (LWR) without plutonium recycle. Dix summarizes his evaluation of the platinum-group fission-product elements by concluding that "in gross terms, our U.S. resources of fission product platinum-family metals will approximate our domestic

needs before the year 2000. We are essentially dependent upon imported supplies of these materials and possess less than 31 million grams of natural domestic reserves of these materials versus requirements of 1.7 billion grams from now until 2000."<sup>4</sup> Dix believes we should consider using some radioactive materials in closed systems, wait for others to decay, and use isotope separation on selected elements.

Deonigi<sup>5</sup> presents the results of detailed calculations of isotope production and availability from power reactors. His case 1 is based on the assumptions that an installed capacity in 1980 will be 150 GW(e), that LWRs will be the only type of reactor installed, and that there will be no uranium or plutonium recycle. The installed capacity, in GW(e), would rise to 296 in 1985 and 500 in 1990. His case 3 is the same as case 1, except that plutonium is recycled. The installed capacity of plutonium recycle would be 26, 68, and 144 GW(e) in 1980, 1985, and 1990 respectively. Thus, by 1990, about one-third of the total installed capacity in case 3 would be plutonium recycle.

The thermal fission of  $^{239}\text{Pu}$  gives a 4.50% yield of the 106 chain compared with a 0.41% yield from  $^{235}\text{U}$  fission. At first glance, this would suggest a tenfold increase in the available  $^{106}\text{Ru}$ , and the resulting  $^{106}\text{Pd}$ , by going to plutonium recycle. In practice, however, such a large increase may not be realizable. Deonigi discusses this point with reference to his calculations. He notes that even with LWRs based on uranium fuel, a significant number of the fissions (on the order of 30%) will be plutonium fissions. Moreover, his plutonium recycle case 3 only arrives at 142 GW(e) out of a total of 500 GW(e) by 1990 because the growth rate of the industry ensures that there would still be a preponderance of nonrecycle fuel over the recycle fuel.

Deonigi tabulates the annual availability of  $^{106}\text{Ru}$  and finds, for case 1, values of 185, 433, and 882 kg per year for 1980, 1985, and 1990 respectively. For his plutonium recycle case 3 he reports 207, 528, and 1130 kg per year. The ground rules used in Deonigi's evaluation included an allowance of one year between reactor discharge and isotope recovery and a 90% recovery of the by-product fission products. If the availability of  $^{106}\text{Ru}$  were measured at reactor discharge, these figures would be doubled. With increases in the amount of plutonium recycle,

further increases in  $^{106}\text{Ru}$  availability can be predicted. It would be interesting to calculate the maximum  $^{106}\text{Ru}$  available at reactor discharge from a reactor system operating entirely on  $^{239}\text{Pu}$  fission, but this calculation is not required to support interest in developing the separation process for application to the practical situations of the next 20 years.

If ruthenium is to be separated from palladium, it is important to estimate where, and in what form, they will appear (or could be made to appear) in the reprocessing flow sheet. A brief review of the reprocessing literature suggests that about 80% of the fission-product ruthenium may appear in the elemental form as an undissolved residue from nitric acid dissolution of  $\text{UO}_2\text{-PuO}_2$  fuel elements.

Bartlett et al.<sup>6</sup> have discussed the identification of solid residues from the dissolution of various fuel elements and report that

"Very few studies have been made to determine the volume and identity of the insoluble residues resulting from the dissolution of various fuel elements. These solids are primarily insoluble cladding oxides and undissolved core materials, such as Mo, Pd, Rh, Nb, Zr, Mn, Al, Ce, Ba, La, Ru, and Si."<sup>6</sup>

Goode<sup>7</sup> found that more than 90% of highly irradiated (99,000 MWD/ton) 20%  $\text{PuO}_2\text{-80% UO}_2$  fast-reactor fuel specimens dissolved in less than 5 h in all concentrations of nitric acid greater than 3 M. Undissolved residues consisted of core oxides and fission-product molybdenum, zirconium, palladium, ruthenium, and rhodium. Gamma-ray scanning showed that nearly all the radioactivity in the residue was due to  $^{106}\text{Ru}$ . Goode and Vaughn<sup>8</sup> made a quantitative study of the dissolution of mechanically blended 25%  $\text{PuO}_2\text{-75% UO}_2$  in boiling 8 M nitric acid for 10 h, followed by leaching for 4 h in 8 M  $\text{HNO}_3\text{-0.05 M HF}$ . The fuel had been irradiated to  $\sim 1.5$  fissions per 100 initial actinide metal atoms present and had decayed 30 d. They reported the dissolution of more than 99% of the plutonium and 99.99% of the uranium, but only a minor fraction ( $\sim 20\%$ ) of the ruthenium.

Musgrave et al.<sup>9</sup> indicate that the ruthenium was about 20% dissolved (i.e., 80% of the ruthenium remained in the residue) as a result of

chemical or electrochemical dissolution of the EBR II (Experimental Breeder Reactor) uranium-fissium alloy, whereas the molybdenum was quantitatively dissolved. Campbell<sup>10</sup> reports that the dissolver residues after nitric acid treatment in conventional LWR fuel reprocessing are the elemental noble-metal fission products. A typical solids composition is 10% to 20% molybdenum, ~2% to 20% technetium, 30% to 50% ruthenium, ~2% to 10% rhodium, and ~10% palladium.

Thus, it seems reasonable to expect that most of the noble-metal fission products can appear as the elements in residues from established dissolution techniques. If serious developmental work on palladium separation were undertaken, it also seems reasonable that different techniques for treatment of the irradiated fuels might give higher yields of the noble metals or might provide them in more convenient forms. For example, treatment of irradiated fuel with a molten metal under very mildly reducing conditions, or after hydrogen reduction, might dissolve the noble metals preferentially. At any rate, it seemed reasonable to start with the elemental metallic state in developing schemes for the separation of palladium from ruthenium.

The following sections of the report indicate that effective palladium-ruthenium separations can very likely be based on solubility in liquid metals, selective intermetallic compound formation, or liquid-liquid partition between pairs of immiscible liquid metals. The final section of the report indicates the possibility of recovering some nonradioactive rhodium from very early reprocessing of spent fuel.

## 2. SOLUBILITY IN LIQUID METALS

Differences in solubility permit the separation of materials by fractional crystallization (or fractional dissolution of the more soluble component). Information available in the literature on solubility suggests that ruthenium and palladium can be easily separated, although no specific demonstration has been reported.

Kerridge,<sup>11</sup> in 1960, surveyed the entire field of the solubility of metals in liquid metals. He tabulated a matrix of 19 solvent metals, each at an appropriate temperature, against 41 solute metals having atomic numbers from 3 (lithium) to 84 (bismuth). No references were given for the solubility values, but he reported they had come from "all published liquidus curves."<sup>11</sup> The only data shown for ruthenium and rhodium were for solubilities in zinc and bismuth; palladium solubility in eleven solvent metals was noted. No information was presented for elements 39 through 43 (yttrium, zirconium, niobium, molybdenum, and technetium). A strong correlation between solubility and position in the periodic table was noted. The best, but still not very good, quantitative correlations were based on the latent heat of fusion of the solute, or, solute lattice energy.

The interest of Brookhaven National Laboratory in a liquid-metal-fueled nuclear reactor led to an important study of fission-product solubilities in molten bismuth. Much of this work was done by Schweitzer and Weeks.<sup>12</sup> Weeks<sup>13</sup> has summarized their work and the work of others. A striking difference in solubility between palladium and ruthenium was found, with palladium being about 100 times as soluble as ruthenium:

$$\log(a/o \text{ Pd}) = 2.95 - 1170/T ;$$

$$\log(a/o \text{ Ru}) = -0.56 - 808/T .$$

Thus, at an appropriate temperature and bismuth:palladium ratio, all the palladium would be dissolved, along with about 1% of the ruthenium. A few cycles of such treatment should provide an adequate separation of the two elements, although the temperature coefficient of solubility is not very high.

Another large program of study of fission-product solubilities in molten zinc was part of Argonne National Laboratory's (ANL) interest in nuclear fuel reprocessing by pyrometallurgical techniques. Johnson and Dillon<sup>14</sup> collected all the available information on the solubility of metals in zinc in 1965. Again, palladium and ruthenium show striking differences:

$$\log(a/o \text{ Pd}) = 4.061 - 3242/T ;$$

$$\log(a/o \text{ Ru}) = 5.905 - 6191/T .$$

The relative differences in solubility are not so great as in the bismuth solvent, but both temperature coefficients are much larger, and that of ruthenium is higher than that of palladium. This could be important from a practical standpoint since a repetition of heating-cooling cycles might be more efficient at freeing all the palladium trapped within any consolidated ruthenium solid. There is no information in the literature to suggest that there are intermetallic compounds of ruthenium and zinc.

Johnson<sup>15</sup> compared the solubilities of metals in zinc and in cadmium and found a strong correlation with atomic number (his value for ruthenium in zinc at 600°C seems to be misplotted as 0.01 instead of 0.1 wt %). He finds very low values for molybdenum and ruthenium, with technetium, in between, estimated as even lower. A later study by Chasanov, Johnson, and Schablaske<sup>16</sup> established technetium solubility in zinc at 600°C as 0.015<sub>6</sub> wt %, lower than molybdenum and ruthenium. (Johnson<sup>17</sup> extended the cadmium solubility studies to include the rare earths and found interesting solubility regularities for the cubic and tetragonal forms of MCd<sub>11</sub> and MCd<sub>6</sub> at 400° and 500°C.)

Moffatt,<sup>18</sup> in 1976, listed binary-phase diagrams of ruthenium with 32 other elements, quite a contrast to the two values in Kerridge's survey 16 years earlier. The ruthenium eutectics with plutonium (10 a/o - 525°C) and uranium (18 a/o - 885°C) are relatively low melting for high concentrations of ruthenium. The high solubility of ruthenium in a uranium-chromium eutectic is relevant to the liquid-liquid extraction discussed below.

A separation process can be visualized based on recrystallization from zinc or bismuth. The zinc and bismuth should be tested for amenability to the mechanical operations required. Other suitable solvents probably could be discovered by an experimental program.

### 3. INTERMETALLIC COMPOUNDS, MUTUAL SOLUBILITY, AND COPRECIPITATION

#### 3.1 Equilibrium Precipitation

In analogy to the solubility product principle of ionic aqueous chemistry, solutions of metallic elements in liquid metals can show mutual solubility effects involving the precipitation of insoluble intermetallic compounds. Smith and Ferris<sup>19</sup> report a quantitative study of the interaction of nickel and thorium in bismuth solutions in which  $[Ni][Th] = K_{\eta}$  (actually bismuth participated in the reaction, which formed  $ThNiBi_2$ , but the bismuth concentration was very high and constant). Under equilibrium conditions, the nickel and thorium concentrations were inversely related, and either could be forced out of solution by the addition of the other.

Similar relationships, in less precise studies, are reported by Dwyer, Howe, and Avrutik<sup>20</sup> for some of the more noble nonvolatile fission products, including ruthenium and palladium, in a study of their removal from uranium-bismuth nuclear reactor fuels. The mutual solubilities of ruthenium and zirconium in bismuth at 500°C showed a strong inverse relationship on the basis of nine additions of zirconium to solutions that initially contained 110, 75, or 55 ppm ruthenium; in every case, after 24 h, the ruthenium content was lowered. No experiments were reported in which ruthenium additions were used to lower the zirconium concentration. The final ruthenium concentrations were as low as 10 ppm when the zirconium level was 150 to 200 ppm. (Magnesium at 100 to 500 ppm was also present to protect the solutes from possible oxidation, and this may have complicated solubility relationships.)

Similar experiments at 500°C showed that titanium was even more effective in removing the ruthenium from solution, but the data do not permit quantitative evaluation. Ruthenium concentrations as low as 2 to 5 ppm appear to have been reached in the presence of 70 to 350 ppm titanium.

Dwyer also reports that, by analogy to the well-known Parkes process for desilverizing bismuth, the addition of as little as 0.3% zinc to the

bismuth was sufficient to lower the selenium, niobium, tellurium, ruthenium, rhodium, and palladium concentrations to about 1 ppm in a single treatment. Dwyer's data do not show any separation of palladium from ruthenium by this treatment, but he does present a few data showing the effects of temperature and zinc concentration on the solubility of palladium in bismuth. These suggest a rather high "solubility product" in which, even at the lowest temperature studied, 270°C, 2500 ppm zinc reduced the palladium concentration to 2 ppm and 5000 ppm zinc reduced it to 1 ppm.

The quantitative study of mutual solubility relationships involving ruthenium, palladium, and rhodium could lead to a better understanding of intermetallic compounds as well as more efficient separation processes. Tests should be made to see whether a process could be based on first precipitating ruthenium from bismuth solution with titanium, followed by the addition of zinc to precipitate the palladium. [Dwyer reports that the remaining zinc can be removed by sparging with chlorine, as in commercial production of bismuth.<sup>20</sup> (Chlorine could also be used to remove traces of titanium prior to the zinc addition, if necessary.)]

### 3.2 Nonequilibrium Precipitation

There are precipitation processes in which a minor (or trace) constituent of a solution is partitioned (or carried) by another precipitate with which it is isostructural. The classic work on this technique was done by Doerner and Hoskins,<sup>21</sup> who used barium sulfate as the carrier and radium as the trace constituent. (It is interesting that they acknowledged the contribution of S. C. Lind, later to become Director of the ORNL Chemistry Division, "who suggested and outlined the problem to be studied and critically reviewed the manuscript.") A mathematical characteristic of this type of precipitation gives rise to a Doerner-Hoskins plot revealing a linear relationship between log fraction carrier remaining in solution and log fraction tracer remaining in solution.

Workers at ANL have used this technique and analysis method in connection with the study of pyrometallurgical methods for fuel reprocessing. Much of their work was directed toward systems including uranium, zinc

or cadmium, and magnesium. Moriarty, Johnson, and Feder<sup>22</sup> give examples of coprecipitation of lanthanum, selenium, praseodymium, samarium, uranium, and thorium with the carrier,  $\text{CeCd}_{11}$ , from liquid cadmium. They point out the importance of tracer insolubility and the formation of isostructural phases as being necessary for coprecipitation.

The coprecipitation of ruthenium with uranium from liquid magnesium-zinc solutions was noted when magnesium was added to precipitate uranium.<sup>23</sup> From phase diagram information it was assumed that  $\beta$ -uranium was the precipitating phase at  $752^\circ\text{C}$  and  $\gamma$ -uranium at  $810^\circ\text{C}$ . The Doerner-Hoskins coefficients were 0.3 and 0.8, respectively, suggesting that  $\gamma$ -uranium was the more effective, but some analytical problems and assumptions about the uranium concentrations clouded the conclusion.

Coprecipitation from the uranium-magnesium-zinc ternary was studied at ANL<sup>23,24</sup> by adding magnesium and then cooling. Cerium, ruthenium, and zirconium were studied: Coprecipitation of ruthenium with  $\alpha$ -,  $\beta$ -, and  $\gamma$ -uranium was indicated, but cerium did not so coprecipitate; zirconium may have been coprecipitated by  $\gamma$ -uranium and/or by formation of a zirconium-uranium intermetallic phase above  $797^\circ\text{C}$ .

ANL workers<sup>25,26</sup> found no coprecipitation of ruthenium with  $\text{U}_2\text{Zn}_{17}$  from molten zinc solution at low concentrations. At tenfold-higher ruthenium concentrations, the equilibrium solubility vs temperature relationship for ruthenium was altered by the presence of uranium.

Other work at ANL,<sup>27</sup> in demonstrations of a skull recovery process connected with melt refining of breeder reactor fuels, showed that a high recovery of noble metals (60% to 99% for ruthenium and palladium) was achieved in a noble-metal extraction step by treatment with zinc and a molten salt flux at  $800^\circ\text{C}$ ; no substantial separation of palladium from ruthenium was shown, and almost no uranium was extracted. In later steps involving the precipitation of  $\text{U}_2\text{Zn}_{23}$  by cooling a zinc-magnesium solution from  $800^\circ$  to  $520^\circ\text{C}$ , little separation of uranium from the residual ruthenium occurred, that is, "the ruthenium apparently coprecipitated extensively with both the uranium-zinc intermetallic compound and uranium metal."<sup>27</sup> Palladium remained in the supernatant in the precipitation steps and apparently did not coprecipitate under these conditions. This report contrasts with an earlier ANL study by Johnson

and Anderson<sup>28</sup> in which it is stated that ruthenium did not coprecipitate with  $U_2Zn_{17}$  from liquid zinc in the temperature range of 700° to 500°C. The designation,  $U_2Zn_{23}$ , in Fig. 5 of the later ANL report,<sup>27</sup> is confusing; published phase diagrams and the work reported by Martin and Wach in the same report<sup>29</sup> indicate that the so-called delta phase,  $U_2Zn_{17}$ , is stable under the reported temperature-composition conditions<sup>27</sup> of 800° to 520°C and excess zinc. Martin and Wach, nevertheless, show both an epsilon and a delta zinc-uranium phase in an experimental photomicrograph, with the epsilon phase being between the zinc and the delta phase, that is, from higher zinc concentrations (formed at 618°C). The epsilon phase was later reported by the same authors<sup>30</sup> to contain 28 wt % uranium; at 650°C, the epsilon phase field was reported to extend from 24.1 to 28.0 wt % uranium and the epsilon plus delta field from 28.0 to 30.0 wt % uranium. (It had previously been established that the delta plus uranium field extends from 30.0 to about 100 wt % uranium.<sup>31</sup>)

In a later study of the zinc-uranium system, Martin and Wach<sup>32</sup> present additional evidence for the existence of a second intermetallic phase, the epsilon phase. They established 790° to 800°C as the temperature at which the epsilon phase decomposes to the delta phase and uranium-saturated melt. Clearly, an understanding of ruthenium coprecipitation from uranium-zinc or uranium-zinc-magnesium systems will require more information about the phases present.

Further study of coprecipitation under nonequilibrium conditions appears less attractive than the other routes examined.

#### 4. LIQUID-LIQUID EXTRACTION

The purification of nuclear-reactor-irradiated fuel by liquid-liquid partition between immiscible liquid metals was reviewed by Voigt in 1955<sup>33</sup> and by Feder and Dillon in 1961.<sup>34</sup> Studies at Ames Laboratory, Chalk River, and Argonne National Laboratory encompass most of the available literature that is relevant to ruthenium-palladium separation. The list of immiscible liquid-metal pairs for which some distribution information has been found includes Mg/(U-5 wt % Cr), Mg/(U-11 wt % Fe), La/U, Ce/U, Ag/U, Nd/U, Ag/(U-Cr), Al/Bi, Ca/U, Ba/U, Pb/Zn, Bi/Zn, and Al/Cd.

The most striking combination of distribution coefficients for ruthenium and palladium so far located is that involving magnesium and the uranium-chromium eutectic. Elliott and Sweezer<sup>35</sup> at ANL report the following:

| Concentration <sup>a</sup> | Temperature<br>(°C) | K <sup>b</sup>          |
|----------------------------|---------------------|-------------------------|
| <i>Palladium</i>           |                     |                         |
| 0.0071                     | 948                 | >10 <sup>2</sup>        |
| 0.0064                     | 937                 | >10 <sup>3</sup>        |
| <i>Ruthenium</i>           |                     |                         |
| 0.042                      | 936                 | 1.7 × 10 <sup>-4</sup>  |
| 0.052                      | 944                 | <3.3 × 10 <sup>-4</sup> |
| 0.114                      | 936                 | 5.6 × 10 <sup>-4</sup>  |

<sup>a</sup>Atom fraction in the preferred phase.

<sup>b</sup>Ratio of atom fraction in magnesium to atom fraction in uranium-chromium.

These distribution coefficients combine to give enormous separation factors of 10<sup>5</sup> to 10<sup>6</sup>, which should permit complete removal of palladium from ruthenium within only one or two contact stages.

Any practical use of this system requires that the palladium and ruthenium have adequate solubilities at the temperatures of contact.

The reported ruthenium concentration 0.114 atom fraction in the uranium-chromium eutectic seems high enough for practicality. Ruthenium is reported to be soluble in magnesium to 20 wt % at 800°C.<sup>36</sup> The magnesium-palladium phase diagram reported in Shunk<sup>37</sup> shows over 40 wt % solubility of palladium at 800°C and about 50 wt % at 1000°C. The uranium-chromium eutectic melts at 870° ± 3°C;<sup>38</sup> magnesium melts at 650°C and boils at 1107°C.

Of the other noble-metal fission products associated with palladium and ruthenium, molybdenum is reported to dissolve in magnesium to the extent of less than  $2 \times 10^{-4}$  wt % at temperatures of 680° to 1000°C;<sup>39</sup> rhodium is reported to have extracted very strongly into magnesium at 942°C and at a concentration of 0.008 atom fraction. No measurement of rhodium solubility in magnesium has been found, but it would be expected to be intermediate between ruthenium and palladium, as it is in zinc;<sup>40</sup> silver and cadmium are reported to extract strongly into magnesium at 930°C<sup>35</sup> and both are extremely soluble in magnesium. Technetium is reported to be insoluble in liquid cadmium at 500°C but soluble in liquid zinc.<sup>41</sup> As previously predicted,<sup>40</sup> the solubility in zinc<sup>16</sup> is at a minimum with respect to the periodic series: 0.015<sub>6</sub> wt % at 600.9°C, but rising to 0.11<sub>8</sub> wt % at 757.5°C and estimated to be about 1.2 wt % at 950°C (technetium is expected, by analogy, to be only slightly soluble in magnesium at temperatures of about 950°C).

A viable separations process can be composed on the basis of the above information:

1. Noble-metal fission-product residues from the LWR head-end dissolution step (in or reduced to the elemental form) are treated with molten magnesium at 950°C; the molybdenum and technetium are insoluble, but ruthenium, rhodium, palladium, silver, and cadmium are soluble. The solution is separated from the insoluble residue.
2. The magnesium solution is contacted with molten uranium-chromium eutectic at 950°C; the ruthenium is extracted from the magnesium to form a 0.10 a/o solution in the uranium-chromium. The phases are separated.

3. The uranium-chromium phase containing the ruthenium may be contacted with a fresh supply of molten magnesium at 950°C to provide additional decontamination from the radioactive palladium. The phases are separated.
4. The uranium-chromium-ruthenium phase is allowed to freeze and is stored for a period of time to permit the  $^{106}\text{Ru} \rightarrow ^{106}\text{Rh} \rightarrow ^{106}\text{Pd}$  decay to occur; then it is heated to 950°C and reextracted with fresh magnesium to remove the  $^{106}\text{Pd}$  (and any traces of  $^{106}\text{Rh}$ ), which produces a solution of nonradioactive palladium in magnesium which can be converted to any desired form. (Any  $^{103}\text{Rh}$  formed by the decay of  $^{103}\text{Ru}$  will also be present in the magnesium solution.)

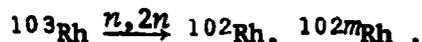
A small advantage may be the shielding provided by the uranium during the storage-decay period.

Choosing appropriate crucible or container materials for the liquid-liquid extraction is a matter of importance. Provow and Fisher<sup>38,42</sup> chose tantalum as a container for electrical resistivity experiments on the uranium-chromium eutectic up to 1000°C and on a molten magnesium-thorium eutectic up to 900°C. They indicate that the uranium-chromium eutectic was contained in both yttrium and tantalum, in tantalum at 950°C for nearly 2000 h, and later circulated in a loop of yttrium tubing at 900° to 1000°C. The eutectic was also melted under vacuum in a magnesia crucible by induction heating in 40-lb melts. The ANL studies of the distribution of fission products between pairs of immiscible metals were performed in 20-g charges in crucibles of tantalum, magnesia, Morganite alumina, and zirconia, with no indication of attack on the crucibles or interference with the experiments.<sup>35</sup>

Although palladium and ruthenium have not yet been separated by the process described above, it seems sufficiently promising to have been chosen for the first experimental tests. Prospects for other liquid-liquid extraction schemes seem to depend on finding experimental or theoretical bases for testing liquid metals that dissolve and preferentially extract ruthenium as well as does uranium or its lower-melting eutectics.

## 5. RECOVERY OF NONRADIOACTIVE RHODIUM

An interesting recovery of nonradioactive rhodium via  $^{103}\text{Ru}$  may be possible if a rhodium-ruthenium separation can be made very soon after the reactor fuel is discharged. Roberts<sup>2</sup> has analyzed the radiation characteristics of reactor-produced rhodium. The principal isotope of rhodium which is formed is stable  $^{103}\text{Rh}$ . Unfortunately, from the standpoint of utilization,  $^{102}\text{Rh}$  and  $^{102m}\text{Rh}$  are also produced by the secondary reaction:



The two isomers of  $^{102}\text{Rh}$  are radioactive, with half-lives of  $3.40 \pm 0.25$  y for  $^{102m}\text{Rh}$ , determined by Roberts, and 206 d for  $^{102}\text{Rh}$ , from the literature. Thus, a considerable time period of decay will be required before ordinary reactor-produced rhodium will reach a level of radioactivity sufficiently low to permit unrestricted use in commercial channels.

If a clean chemical separation of rhodium from ruthenium can be made very soon after reactor discharge of the spent fuel, some 39.8-d  $^{103}\text{Ru}$  will be present, along with larger amounts of 368-d  $^{106}\text{Ru}$ . The  $^{103}\text{Ru}$  will decay to  $^{103}\text{Rh}$ , which has a 57m internal transition to the stable  $^{103}\text{Rh}$ . The 103-chain yields from fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$  are both higher than the 106-chain yields; for  $^{235}\text{U}$ , the 2.9% yield is almost tenfold greater, thus partially compensating for the much shorter half-life of  $^{103}\text{Ru}$  as compared with  $^{106}\text{Ru}$ .

Fortunately, the same liquid-liquid extraction process that is favored for removing radioactive palladium from ruthenium should also remove the radioactive rhodium. Elliott and Sweezer<sup>35</sup> reported that rhodium extracted strongly (essentially total extraction) into magnesium from the uranium-5 wt % chromium eutectic at 942° to 944°C (at concentrations of 0.0046 and 0.0080 atom fraction rhodium in the magnesium phase, with a 10:1 mole ratio of magnesium and contained in a magnesium oxide crucible).

The recovery of ordinary fission-product rhodium and the potential for its use in restricted or nonrestricted channels after decay have

been evaluated by Clark et al.<sup>3</sup> The most significant new items relating to rhodium in general are its use in automobile exhaust catalysts and as a vapor plating coating for jewelry. The price of rhodium has increased sharply from \$4 per gram in 1955 to \$10 per gram in 1974 and \$15 per gram in 1978. All fission-product wastes that have been stored for more than 25 to 30 years should be considered candidate materials for rhodium recovery as a consequence of the decay of the 3.4-y  $^{102m}\text{Rh}$ , the longest-lived rhodium isotope in these wastes.

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