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Recovery of Nonradioactive Palladium and Rhodium from Radioactive Waste

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ABSTRACT

The U.S. production of palladium has not exceeded 1000 kg per year while consumption has reached 46,000 kg per year. At the Oak Ridge National Laboratory, we have demonstrated the technical feasibility of a process that could be used to recover over 2000 kg per year of nonradioactive palladium and rhodium each from radioactive nuclear waste. The method is based on an essentially complete removal of ruthenium (the precursor of nonradioactive Pd and Rh) from the radioactive palladium and rhodium. Decay of 368-d ^{106}Ru and its 30-s ^{106}Rh daughter produces nonradioactive ^{106}Pd while decay of 40-d ^{103}Ru yields nonradioactive ^{103}Rh. After an appropriate waiting period for the decay, separation of this nonradioactive palladium and rhodium from the remaining ^{106}Ru gives a product suitable for unrestricted commercial use. Several liquid metal extraction and partitioning systems have been investigated which give the required ruthenium-palladium-rhodium separation. For example, when molten magnesium containing 0.1 at. % each of palladium and ruthenium was equilibrated with molten uranium-5 wt % chromium eutectic at 900°C, the ruthenium extracted into the uranium-chromium solution while the palladium remained in the magnesium. Separation factors of greater than 10^6 were obtained.

INTRODUCTION

The United States has never been a large producer of palladium or rhodium. In 1966, palladium production reached a high of 901 kg; in 1973, 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 and rhodium has been much greater than the amount produced: in 1974, 46,587 kg of palladium was used; there are increased demands in the automotive and dental industries. Thus, the United States is in an economically and strategically uncomfortable position with respect to palladium and rhodium even though there is a substantial stockpile.

Most attempts to recover valuable products from irradiated nuclear reactor fuels have dealt with the recovery and use of radioactive isotopes (1-3). Reexamination of the possibilities for beneficial recovery of fission-product materials at the Oak Ridge National Laboratory has revealed a fortuitous combination of nuclear and chemical properties that makes it possible to recover appreciable quantities of nonradioactive palladium and rhodium from fission-product residues (4). The method is based on an essentially complete removal of ruthenium (the precursor of nonradioactive Pd and Rh) from the radioactive palladium and rhodium. Decay of 369-d ^{106}Ru and its 30-s ^{106}Rh daughter produces nonradioactive ^{106}Pd while decay of 40-d ^{103}Ru yields nonradioactive ^{103}Rh. After an appropriate waiting period for the decay, separation of this nonradioactive palladium and rhodium from the remaining ^{106}Ru and ^{103}Ru gives a product suitable for unrestricted commercial use.

G. P. Dix (5) estimated that, in 1990, 2000 kg of ^{106}Ru would be available from spent nuclear fuel. This estimate was based on an installed nuclear generating capacity of 400 GW(e), which considered only U. S. civilian reactors and light-water reactors (LWR) without plutonium recycle. With increases in the amount of plutonium recycle an increase in ^{106}Ru availability

was predicted (6). The nuclear fission yield of ^{103}Ru (the precursor of ^{103}Rh) is almost ten times greater than the yield of ^{106}Ru (the precursor of ^{106}Pd). However, because of the much shorter half-life of ^{103}Ru (39.8 d) as compared with ^{106}Ru (368 d) the concentrations of ^{103}Ru will be considerably less than the concentrations of ^{106}Ru at the time of isotope recovery, about 90 days after reactor discharge.

If ruthenium is to be separated from palladium and rhodium, 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 UO_2-PuO_2 LMFBR fuel elements (7-10). The undissolved residue from LWR fuel will contain between 25 and 80% of the total ruthenium depending on fuel element treatment (11). Campbell (11) reports that the dissolver residues from conventional LWR fuel reprocessing with nitric acid 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. This paper reports on several liquid metal dissolution and partitioning systems which utilize these residues.

The purification of nuclear-reactor-irradiated fuel by liquid-liquid partition between immiscible liquid metals was reviewed by Voigt in 1955 (12) and by Feder and Dillon in 1961 (13). The list of immiscible liquid-metal pairs for which some distribution information relating to palladium, rhodium and/or ruthenium 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 reported for ruthenium and palladium is that involving magnesium and the uranium-chromium eutectic. Elliott and Sweezer (14) report the distribution coefficient of palladium (ratio of atom

fraction in magnesium to atom fraction in uranium-chromium) as $>10^2$ and ruthenium as $\sim 5 \times 10^{-4}$. No measurement of the palladium-ruthenium separation factor is reported; however, these distribution coefficients combine to predict a palladium-ruthenium separation factor of $>10^6$.

Inspection of the binary phase diagrams for the Pd-Al, Pd-Bi, Ru-Al, Ru-Bi, and Al-Bi systems suggested that the liquid aluminum-liquid bismuth system might be useful for separating palladium and ruthenium. Ruthenium is reported to distribute quantitatively to the aluminum phase (13). No distribution data are available for palladium. Ruthenium has very low solubility and forms no compounds with bismuth while exhibiting high solubility and forming numerous intermetallic compounds with Al. Palladium and rhodium have high solubility in both liquid aluminum and liquid bismuth and form similar intermetallics with aluminum and bismuth. Therefore, palladium might distribute between the aluminum and bismuth while ruthenium would report to the aluminum phase.

EXPERIMENTAL

The distribution of palladium and ruthenium between immiscible liquid metals was investigated using the experimental apparatus and filtration sampling technique described elsewhere (15, 16). The system was contained under an argon atmosphere. The uranium-chromium eutectic vs. liquid magnesium and the uranium-iron eutectic vs. liquid magnesium equilibrations were carried out in tantalum crucibles. Al_2O_3 crucibles were used for the experiments with liquid aluminum-liquid bismuth. All metals were 99.99 wt % pure grade or greater. Equal number of moles of the immiscible metals or alloys was melted together. The palladium and ruthenium were added as metals in small portions. After each addition and/or temperature change at least four hours were allowed for the attainment of equilibrium before filtered samples of the two liquid phases were taken for analysis. Both atomic absorption and x-ray fluorescence were used in analysis.

RESULTS

Experimental results for the ruthenium-palladium separation by liquid-liquid partitioning between immiscible liquid metals are shown in Table 1 and are in good agreement with the distribution data from the literature (14). For example, when molten magnesium containing ~0.1 at. % each of palladium and ruthenium was equilibrated with molten uranium-5 wt % chromium eutectic at 900°C, the ruthenium extracted into the uranium-chromium solution while the palladium remained in the magnesium. Separation factors of greater than 10^6 were obtained. Although providing good separations, this system has the disadvantages of requiring a high temperature, >900°C. This causes volatilization of magnesium and limits the availability of suitable container materials. Substitution of uranium-iron eutectic (89-11 wt %; mp = 725°C) for the uranium-chromium eutectic (95-5 wt %; mp = 859°C) allows for equilibration at temperatures as low as 750°C with a decrease of magnesium vapor pressure from about 100 mm to 10 mm. Ruthenium-palladium separation factors of $>10^6$ are again obtained. Preliminary experimental measurements indicate that rhodium behaves similarly to palladium in these systems and therefore can also be separated from ruthenium with this system. The distribution of palladium and ruthenium between liquid aluminum-liquid bismuth was measured at several temperatures between 700 and 900°C. It was observed (Table 1) that both the palladium and ruthenium essentially dissolved in the aluminum phase with little reporting to the bismuth. Thus, the aluminum-bismuth binary system does not appear promising for achieving the necessary separations for recovery of palladium and rhodium from nuclear waste.

CONCLUSION

On the basis of information in the literature and the data obtained in this work, we can propose a tentative but viable separation process for recovering non-radioactive palladium and

TABLE 1
The Partitioning of Palladium and Ruthenium Between Two Immiscible Liquid Metal Systems

Temp (°C)	Equilibrium Concentration (atom fraction)				Partition Ratio[a]		Pd:Ru Separation Factor
	Ru	Pd	Ru	Pd	Ru	Pd	
	Mg Phase		U-5 wt % Cr Phase				
900	$<1 \times 10^{-7}$	9.9×10^{-5}	1.1×10^{-4}	$<1 \times 10^{-7}$	$<10^{-3}$	$>10^{3}$	$>10^{6}$
900	3.0×10^{-7}	1.1×10^{-3}	1.3×10^{-4}	1.6×10^{-6}	2.3×10^{-4}	6.9×10^{2}	3.0×10^{6}
950	4.9×10^{-7}	1.2×10^{-3}	1.7×10^{-3}	2.1×10^{-6}	2.9×10^{-4}	5.7×10^{2}	1.9×10^{6}
	Mg Phase		U-11 wt % Fe Phase				
750	$<1 \times 10^{-7}$	1.0×10^{-4}	3.6×10^{-4}	$<10^{-7}$	2.3×10^{-4}	$>10^{3}$	$>10^{6}$
750	9.1×10^{-7}	1.7×10^{-3}	2.4×10^{-3}	1.4×10^{-6}	3.8×10^{-4}	1.2×10^{3}	6.5×10^{6}
800	6.0×10^{-7}	1.8×10^{-3}	2.6×10^{-3}	1.5×10^{-6}	2.3×10^{-4}	1.2×10^{3}	5.2×10^{6}
850	6.7×10^{-7}	1.7×10^{-3}	2.6×10^{-3}	1.5×10^{-6}	2.6×10^{-4}	1.1×10^{3}	4.2×10^{6}
	Al Phase		Bi Phase				
700	1.1×10^{-3}	1.0×10^{-3}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	
700	2.0×10^{-2}	1.9×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	Not
750	2.0×10^{-2}	2.0×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	Measurable
800	1.8×10^{-2}	1.8×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	
850	2.1×10^{-2}	2.0×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	
900	2.0×10^{-2}	1.9×10^{-2}	$<10^{-7}$	$<10^{-7}$	$>10^{10}$	$>10^{10}$	

[a]Concentration in light phase divided by concentration in heavy phase

rhodium from radioactive waste. This process would consist of the following steps.

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; molybdenum and technetium are insoluble, but ruthenium, rhodium, palladium, silver, and cadmium are expected to be soluble. The molten magnesium solution is separated from the insoluble residue.
2. The magnesium solution is then contacted with molten uranium-chromium eutectic at 950°C, or uranium-iron eutectic at 750°C; the ruthenium is extracted from the magnesium to form a 0.10 at. % solution in the uranium alloy phase. The phases are separated.
3. The uranium eutectic 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 and rhodium. The phases are separated.
4. The uranium eutectic ruthenium phase is allowed to freeze and is stored for a period of time to permit the $^{106}Ru \rightarrow {}^{106}Pd$ and $^{103}Ru \rightarrow {}^{103}Rh$ decay to occur; then it is heated, and reextracted with fresh magnesium to remove the ^{106}Pd and ^{103}Rh. This produces a solution of nonradioactive palladium and rhodium in magnesium. The separation and recovery of the palladium and rhodium can then be accomplished by conventional methods.

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