Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Palladium from a Simulated Radioactive Liquid Waste by Precipitation Using Ascorbic Acid

Sung Ho Lee[a]; Chong Hun Jung[a]; Jong Sik Shon[a]; Hongsuk Chung[a]
[a] KOREA ATOMIC ENERGY RESEARCH INSTITUTE, TAEJON, SOUTH KOREA

To cite this Article Lee, Sung Ho , Jung, Chong Hun , Shon, Jong Sik and Chung, Hongsuk(2000) 'Separation of Palladium from a Simulated Radioactive Liquid Waste by Precipitation Using Ascorbic Acid', Separation Science and Technology, 35: 3, 411 — 420

To link to this Article: DOI: 10.1081/SS-100100165

URL: http://dx.doi.org/10.1081/SS-100100165

SEPARATION SCIENCE AND TECHNOLOGY, **35**(3), pp. 411–420, 2000

Separation of Palladium from a Simulated Radioactive Liquid Waste by Precipitation Using Ascorbic Acid

---

SUNG HO LEE,* CHONG HUN JUNG, JONG SIK SHON, and
HONGSUK CHUNG
KOREA ATOMIC ENERGY RESEARCH INSTITUTE
P.O. BOX 105, YUSONG, TAEJON 305-600, SOUTH KOREA

ABSTRACT

The separation characteristics of palladium (Pd) from a simulated radwaste solution by ascorbic acid was investigated. Pd was selectively precipitated by the reduction reaction of Pd with ascorbic acid. For a 1-component system with only Pd, over 99.9% Pd was precipitated at ascorbic acid concentrations above 0.025 M. When the nitric acid concentration in a 7-components system (Pd, Rh, Ru, Fe, Mo, Cs, Sr) was below 2.0 M, Pd over 99.5% was selectively precipitated at an ascorbic acid concentration above 0.06 M while the other elements mainly remained in the solution. As the nitric acid concentration in the simulated solution increases, the precipitation yields of Pd decrease. Pd precipitates formed by ascorbic acid were confirmed as Pd metal from XRD analysis results.

Key Words. Palladium; Ascorbic acid; Precipitation; Reduction; Platinum group metals; Radioactive liquid waste

INTRODUCTION

The platinum group metals (PGM) are valuable and important as noble metals but their natural resources are rather limited. Three of the PGM, palladium (Pd), rhodium (Rh), and ruthenium (Ru), are produced as fission products in nuclear reactors (1). These metals are used for catalytic processes, electronic and electrochemical industries, anticorrosion alloys, dental applications, etc. The demand for noble metals continues to grow steadily.

---

* To whom correspondence should be addressed.

www.dekker.com

As the number of nuclear power plants increases, the amounts of these metals artificially produced are becoming comparable to the amounts available as natural resources. The noble metals generated by fission, can thus be recognized as an important alternative resource toward meeting the increasing need for noble metals (2).

In order to separate the PGM from high-level radioactive liquid waste (HLLW), many recovery methods have been studied, for example, lead oxide extraction method; liquid–liquid extraction method with tributyl phosphate (TBP); adsorption method with active carbon; ion-exchange method; and precipitation methods by formic acid, hydrazine, hypophosphorous acid, and ascorbic acid; etc. (3–7). In the case of precipitation methods by formic acid or hypophosphorous acid, some metals are coprecipitated with Pd (2). However, Pd was selectively precipitated by ascorbic acid. In the present study the precipitation characteristics of Pd by ascorbic acid from simulated radwaste solutions which contained 1, 3, and 7 components were investigated.

EXPERIMENTAL

The simulated radwaste solution used in this study was composed of 1 component (Pd), 3 components (Pd, Rh, Ru), or 7 components (Pd, Rh, Ru, Fe, Mo, Cs, Sr), formulated as representative elements of HLLW. Their concentrations were adjusted to the concentrations listed in Table 1, based on the composition of the supernatant liquor obtained after denitration of the estimated HLLW from the first cycle of the Purex process for PWR spent fuel with 28,000 MWd/MT and 5 year cooling time (8). As shown in Table 1, the number of the elements contained in real HLLW is more than 30. However, elements such as Cr, Cd, Ag, and so on were not added to the simulated solution because their concentrations are low and their presence may not affect the precipitation behavior of Pd in the solution. In particular, it was reported that most Zr and Mo can be removed during denitration of HLLW (8). Zr was deleted and a small amount of Mo was included into the simulated solution used in this study. The recovery step of PGM is generally arranged after the first denitration step (2). Therefore, representative elements in the simulated solution for this study were as follows: Pd, Rh, and Ru for PGM; Cs and Sr for alkali and alkaline earth metals; Fe and Mo for transition metals.

The simulated solution was prepared by dissolving the nitrate salts of each metal, e.g., Pd(II), Ru(IV), and Rh(III). Most chemical reagents for the simulated solution were used in a nitrate salt form, except for Mo which was of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in nitric acid. The nitric acid and ascorbic acid used were of reagent grade.

For this experiment, ascorbic acid was added to the simulated solution in a 15-mL centrifuge tube at room temperature, and then the solution was well

TABLE 1
Chemical Compositions of the Estimated and the Simulated HLLW

Element	Estimated HLLW (mol/L)	Simulated HLLW (mol/L)	Element	Estimated HLLW (mol/L)	Simulated HLLW (mol/L)
Pd	0.018	0.018	Nd	0.0434	—
Rh	0.008	0.008	La	0.0147	—
Ru	0.034	0.034	Ce	0.033	—
Cs	0.037	0.037	Pr	0.0137	—
Na	0.076	—	Pm	0.0012	—
Rb	0.0074	—	Sm	0.0086	—
Sr	0.0167	0.0167	Eu	0.0019	—
Ba	0.0207	—	Gd	0.001	—
Fe	0.038	0.0232	Y	0.0084	—
Cr	0.0091	—	Am	0.0012	—
Ni	0.006	—	Cm	0.00025	—
Mo	0.069	0.0099	U	0.0076	—
Tc	0.015	—	Pu	0.00095	—
Zr	0.069	—	Np	0.0015	—
Ag	0.0009	—	PO_4	0.0023	—
Te	0.0068	—	SiO_3	0.0076	—
Cd	0.0009	—	H+	2	0.1–4

mixed with a vortex mixer (Model Fisher type 37600) for 5 minutes and allowed to stand for 2 hours. Then the two phases were separated using a centrifuge and a 1.0-μm cellulose membrane filter (Whatman). The concentration ranges of nitric acid and ascorbic acid used in the experiments were 0.1 to 4 M and 0.01 to 0.14 M, respectively. The concentrations of Pd, Rh, and Ru in the sample solution were analyzed by inductively couple plasma atomic emission spectroscopy (ICP, Model ISA Jobin-Yvon JY 50P and ISA Jobin-Yvon JY 38 PLUS). The concentrations of Mo, Fe, Cs, and Sr were determined by a flame atomic absorption spectrophotometer (AAS, Perkin-Elmer, Model 3100). The Pd precipitates formed by ascorbic acid were examined by an x-ray diffractor (XRD, Model SIEMENS D5000) and a scanning electron microscope (SEM: JEOL, JSN-5200, Japan).

RESULTS AND DISCUSSION

The redox reaction between the ascorbic acid (H_2A: $C_6H_6O_6$) and dehydroascorbic acid (A: $C_6H_6O_6$) couple in acidic solution is expressed as (9):

$$A + 2H^+ + 2e \xleftrightarrow{\text{couple}} H_2A, \qquad +0.4 \text{ (potential, V)}$$

TABLE 2
Redox System of each Element and Reduction Chemical Reaction by Ascorbic Acid (9)

Elements	Oxidation–reduction system	Standard potential (V)	Reduction chemical reaction	Value of potential (V)
Pd	$Pd^{2+} + 2e \leftrightarrow Pd(s)$	+0.951	$Pd^{2+} + H_2A \leftrightarrow Pd(s) + A + 2H^+$	+0.551
Rh	$Rh^{3+} + 3e \leftrightarrow Rh(s)$	+0.76	$2Rh^{3+} + 3H_2A \leftrightarrow Rh(s) + 3A + 6H^+$	+0.34
Ru	$Ru^{4+} + e \leftrightarrow Ru^{3+}$	+0.908	$2Ru^{4+} + H_2A \leftrightarrow 2Ru^{3+} + A + 2H^+$	+0.508
Fe	$Fe^{3+} + e \leftrightarrow Fe^{2+}$	+0.771	$2Fe^{3+} + H_2A \leftrightarrow 2Fe^{2+} + A + 2H^+$	+0.371
Mo	$MoO_2^{2+} + 2H^+ + e \leftrightarrow MoO_2^{3+}$	+0.48	$2MoO_2^{2+} + 2H^+ + H_2A \leftrightarrow 2MoO^{3+} + A$	+0.08
Sr	$Sr^{2+} + 2e \leftrightarrow Sr(s)$	−2.89	$Sr^{2+} + H_2A \leftrightarrow Sr(s) + A + 2H^+$	−3.41
Cs	$Cs^{+} + e \leftrightarrow Cs(s)$	−2.92	$2Cs^{2+} + H_2A \leftrightarrow Cs(s) + A + 2H^+$	−3.32

The redox system and reduction reactions by ascorbic acid of the elements used in this study are shown in Table 2. From the reduction potential of Pd by ascorbic acid in Table 2, it is clear that Pd can be precipitated by the reduction of Pd^{+2} to Pd metal as in the following reduction reaction:

$$Pd^{2+} + H_2A \leftrightarrow Pd(s) + A + 2H^+, \qquad +0.551 \text{ (potential, V)}$$

The precipitation characteristic of Pd by ascorbic acid in 0.5 M nitric acid in a 1-component system is shown in Fig. 1: as the ascorbic acid concentration

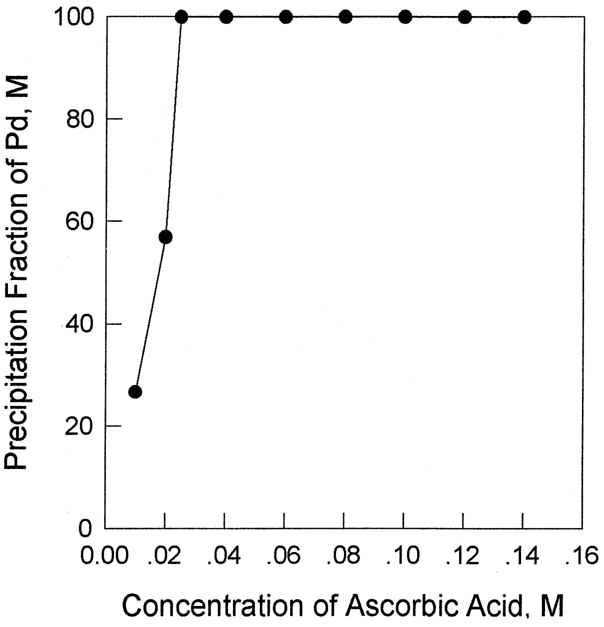

FIG. 1 Precipitation fraction of palladium with the concentration of ascorbic acid in a 1-component system [HNO_3 concentration: 0.5 M].

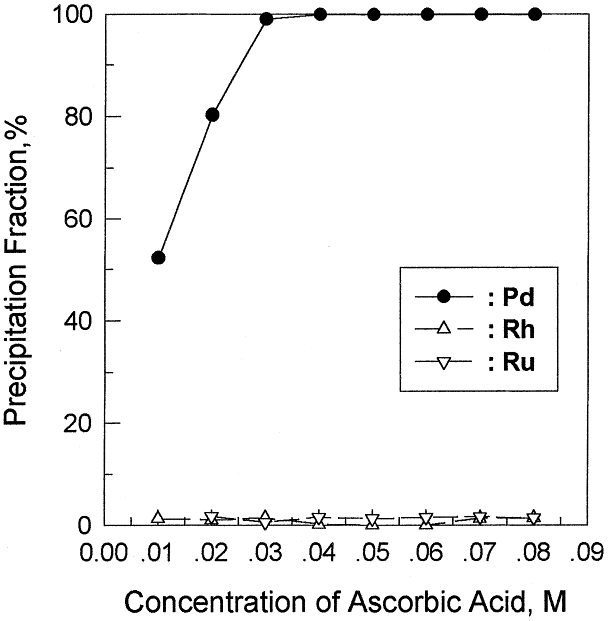

FIG. 2 Precipitation fraction of each element with the concentration of ascorbic acid in a 3-components system [HNO_3 concentration: 0.5 M].

increases, the precipitation yield of Pd increases. Over 99.9% Pd was precipitated at ascorbic acid concentrations above 0.025 M. Figure 2 shows the precipitation characteristics of 3 elements with ascorbic acid concentration in 0.5 M nitric acid. From the results, over 99.9% Pd was quantitatively precipitated at ascorbic acid concentrations above 0.03 M while the other elements mainly remained in the solution. Based on the reduction potential of Rh by ascorbic acid, Rh can also be precipitated; however, Rh was not precipitated at all. From this result it is supposed that more activation energy may be required for the complete reduction of Rh.

Based on the reduction potential of Ru by ascorbic acid in Table 2, it is apparent that Ru^{4+} may be reduced to Ru^{3+} by ascorbic acid, and Rh is also a reducible element by ascorbic acid. Therefore, it is estimated that the required ascorbic acid concentration in the 3-components system is more than that in a 1-component system for the same yield of Pd precipitate. The precipitation characteristics of each element with the concentration of ascorbic acid in 0.1 and 0.5 M nitric acid are shown in Figs. 3 and 4. From the results, Pd was selectively precipitated with an increase of the ascorbic acid concentration while the other elements were scarcely precipitated. Over 99.5% Pd was precipitated at an ascorbic acid concentration above 0.04 M. On the other hand, the ascorbic acid concentration required for the complete reduction of elements in-

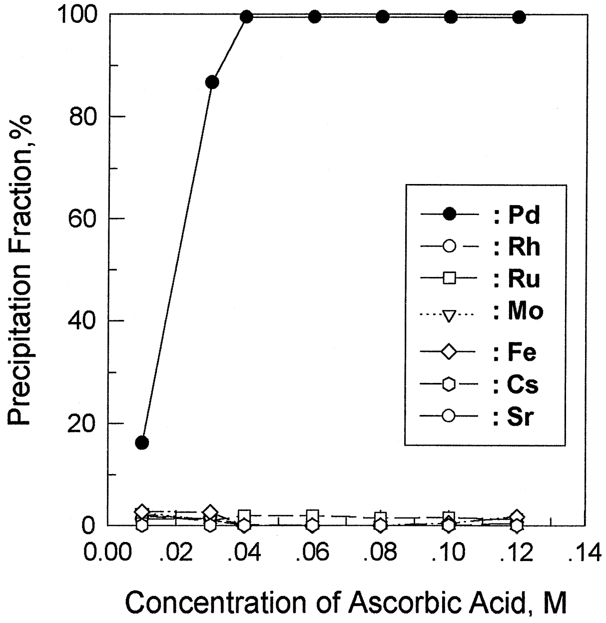

FIG. 3 Precipitation fraction of each element with the concentration of ascorbic acid in a 7-components system [HNO_3 concentration: 0.1 M].

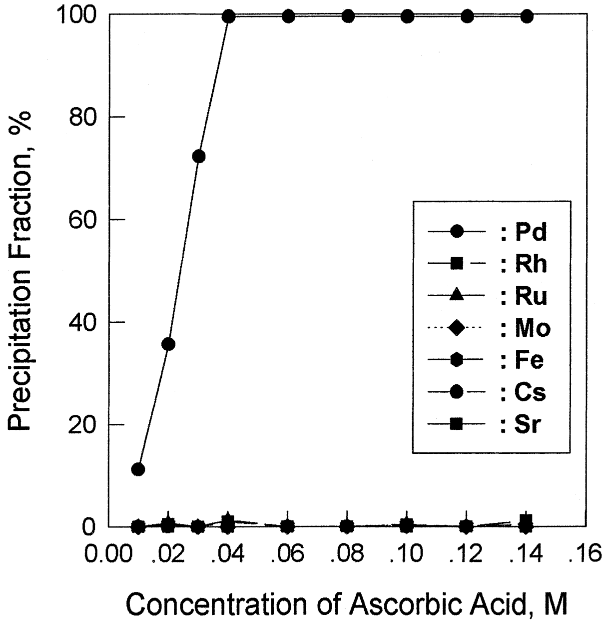

FIG. 4 Precipitation fraction of each element with the concentration of ascorbic acid in a 7-components system [HNO_3 concentration: 0.5 M].

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

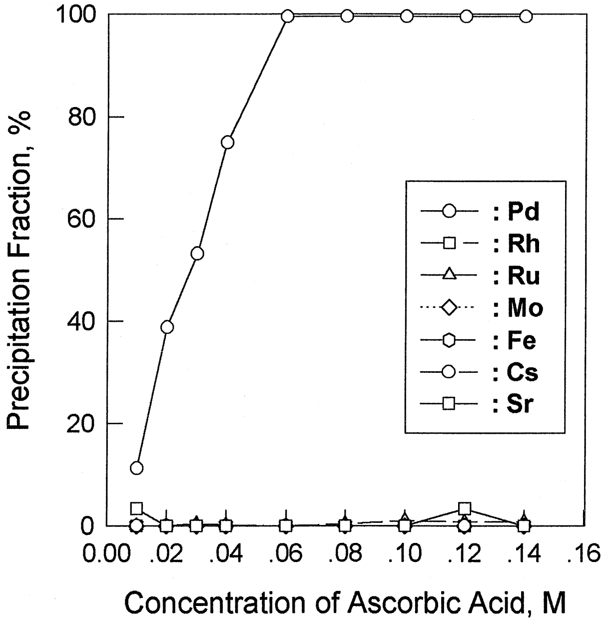

FIG. 5 Precipitation fraction of each element with the concentration of ascorbic acid in a 7-components system [HNO_3 concentration: 2.0 M].

creased because of the presence of metals reducible by ascorbic acid such as Ru, Rh, and Fe. Figure 5 also shows the precipitation characteristics of Pd with the ascorbic acid in 2.0 M nitric acid. As shown in Figs. 3 and 4, as the ascorbic acid concentration increases, the precipitation yield of Pd increases. Pd was quantitatively precipitated at ascorbic acid concentrations above 0.06 M while other elements mainly remained in solution. Over 99.5% Pd was precipitated at an ascorbic acid concentration above 0.06 M. Figure 6 shows the dependency of the precipitation yield of Pd on the nitric acid concentration in a 3-components system. The yield of Pd precipitation was found to be inversely proportional to the nitric acid concentration. Based on this result and the positive reduction potential of nitrate ion (NO_3^-) (10), it is likely that NO_3 in the nitric acid solution may be reduced to nitrite (NO_2^-) ion or nitrosyl (NO^-) ion by the ascorbic acid. Therefore, as the nitric acid concentration increases, the yield of Pd precipitation decreases, and a greater quantity of ascorbic acid is required for complete reduction of elements.

To investigate the characteristics of Pd precipitates formed by ascorbic acid, XRD and SEM analyses were carried out. Based on the XRD and SEM results shown in Figs. 7 and 8, it was confirmed that the Pd precipitate was Pd metal made up of aggregated particles of less than 0.1 μm due to a fast reduction reaction.

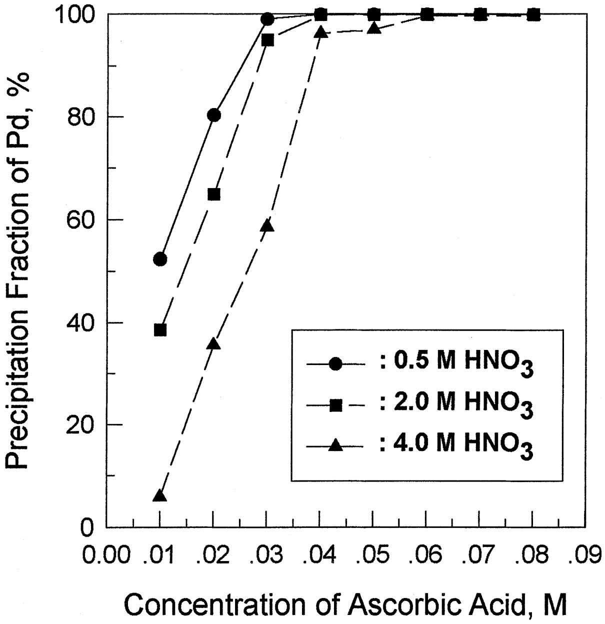

FIG. 6 Effect of nitric acid concentration on precipitation yield of Pd by ascorbic acid in a 3-components system.

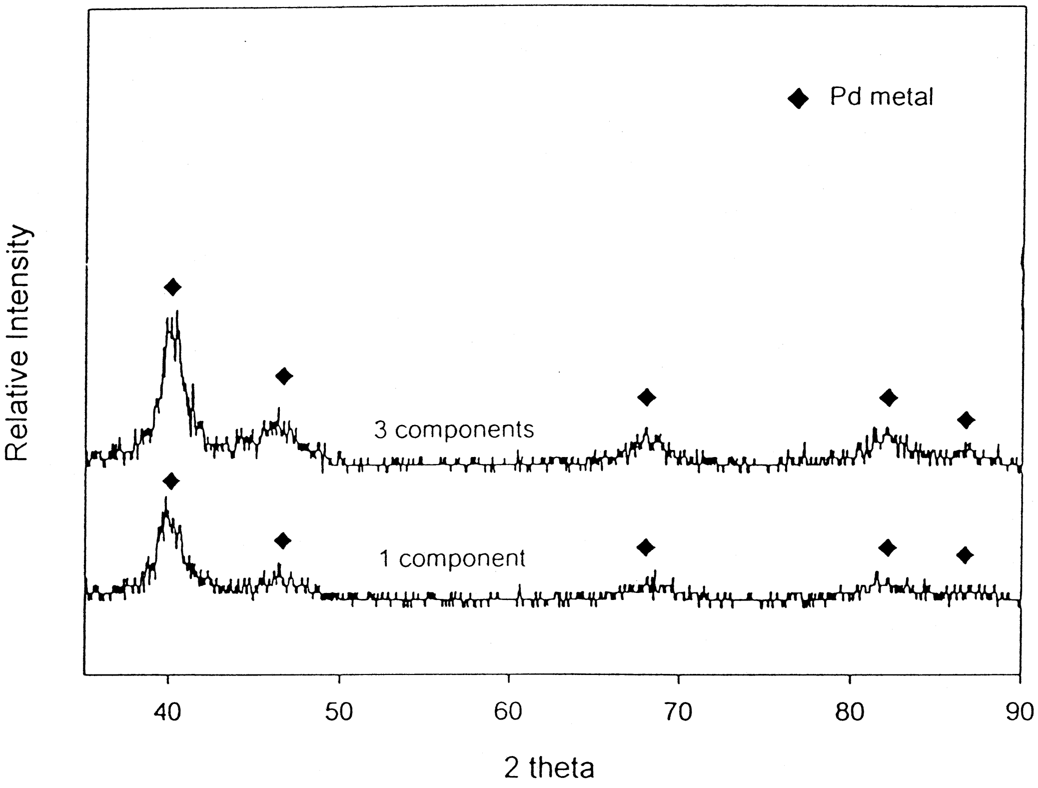

FIG. 7 XRD pattern of Pd precipitates in 1 and 3 components systems.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

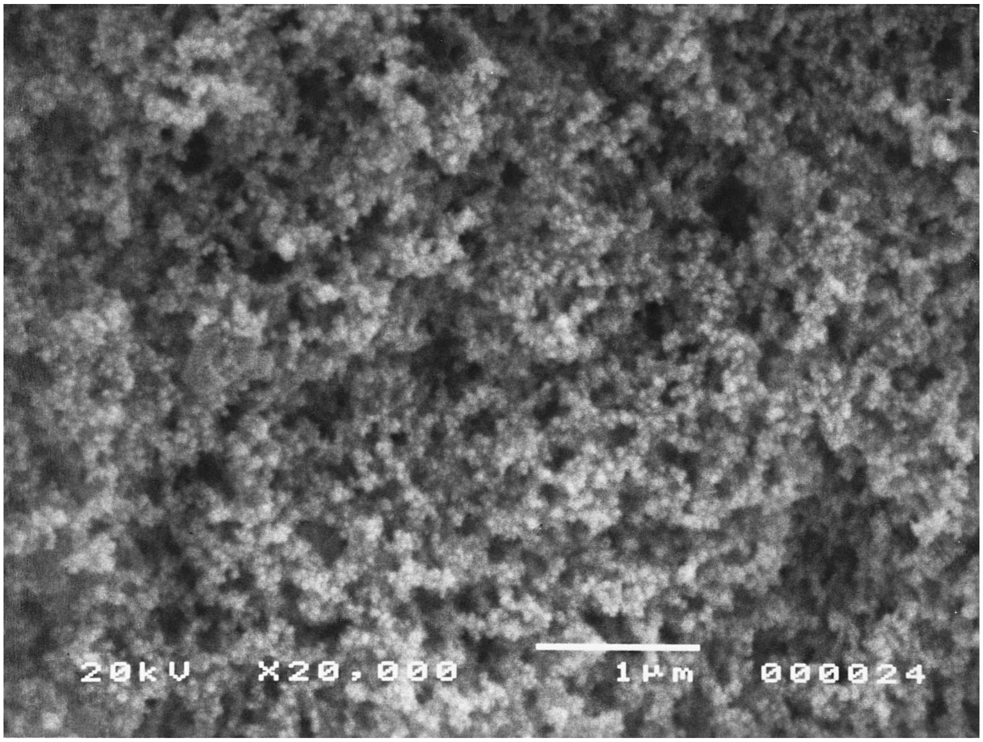

FIG. 8 SEM photograph of Pd precipitate in a 3-components system.

CONCLUSIONS

The precipitation characteristics of Pd by ascorbic acid in a simulated radwaste solution were investigated. Pd was selectively precipitated by the reduction reaction of Pd with ascorbic acid. Over 99.9% Pd in 1- and 3-component systems in 0.5 M nitric acid was quantitatively precipitated at concentrations of ascorbic acid above 0.025 and 0.03 M, respectively. Over 99.5% Pd was selectively precipitated by an ascorbic acid concentration above 0.06 M when the nitric acid concentration of a 7-component system was below 2.0 M, while other elements mainly remained in solution. As the nitric acid concentration in the simulated solution increases, the precipitation yields of Pd decrease and the concentration of ascorbic acid required for complete reduction of elements increases.

XRD and SEM analyses of the Pd precipitates formed by ascorbic acid confirmed that they were Pd metal and made up of aggregated particles of less than 0.1 μm due to a fast reduction reaction. It is assumed that Pd precipitate has a purity over 99% because Pd is selectively precipitated by ascorbic acid from the simulated radwaste solution and exists in a metal form.

Based on these experimental results, Pd can be easily and selectively separated from a simulated radwaste solution by ascorbic acid.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

ACKNOWLEDGMENT

This project has been carried out under the Nuclear R&D Program by MOST.

REFERENCES

1. F. P. Roberts, *The Radiation Characteristics of Reactor Produced Rhodium, Palladium, Ruthenium and Technetium*, BNWL-1693, 1972.
2. Y. Kondo and M. Kuboto, "Precipitation Behavior of Platinum Group Metals from Simulated High Level Liquid Waste in Sequential Denitration Process," *J. Nucl. Sci. Technol.*, *29*(2), 140 (1992).
3. H. F. McDuffie, *Recovery of Nonradioactive Palladium and Rhodium from High-level Radioactive Wastes*, ORNI/TM-6654, 1979.
4. H. Sakurai and K. Hirokawa, "Precipitation Behavior of Metallic Palladium and Platinum in Aqueous Solutions," *Bunseki Kagaku*, *45*(8), 795 (1996).
5. S. J. Al-Bazi and A. Chow, "Platinum Metals-Solution Chemistry and Separation Methods (Ion Exchange and Solvent Extraction)," *Talanta*, *31*(10A), 815 (1984).
6. G. V. Myasoedova and S. B. Savvin, "New Chelating Sorbents for Noble Metals," *Ibid.*, *32*(12), 1105 (1985).
7. J. D. Navratil, "Ion Exchange Technology in Spent Fuel Reprocessing," *J. Nucl. Sci. Technol.*, *26*(8), 735 (1989).
8. M. Kubota and T. Fukase, "Formation of Precipitate in High-level Waste from Nuclear Fuel Reprocessing," *Ibid.*, *17*(10), 783 (1980).
9. C. Creutz, "The Complexities of Ascorbate as a Reducing Agent," *Inorg. Chem*, *20*, 4449 (1981).
10. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 72nd ed., CRC Press, Boston, MA, 1991.

Received by editor January 8, 1999
Revision received May 1999

Downloaded At: 11:02 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS100100165