PRECIPITATION CHARACTERISTICS OF PALLADIUM FROM A SIMULATED RADIOACTIVE LIQUID WASTE BY ASCORBIC ACID

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Abstract–The precipitation 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. When the nitric acid concentration in the 8 component system was below 2.0 M, Pd over 99.5 % was selectively precipitated at an ascorbic acid concentration above 0.06 M, while other elements mainly remained in solution. The precipitation yield of Pd by ascorbic acid decreased with the increase of the nitric acid concentration.

Key words : Palladium, Ascorbic Acid, Radioactive Liquid Waste, Reduction, Precipitation

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 [Roberts, 1972]. These metals are used for catalytic processes, in the electronic and electrochemical industries, anti-corrosion alloys, dental applications etc. The demand for noble metals continues to grow steadily. As the number of nuclear power plants increases, the amounts of these metals are likely to become comparable to those of the natural resources in the world. The noble metals generated by fission can be recognized as important alternative resources to meet the increasing needs of noble metals [Kondo and Kubota, 1992].

In order to separate the platinum group metals from high level liquid wastes (HLLW), many recovery methods for platinum group metals have been studied : for example, lead oxide extraction, liquid-liquid extraction with tri-butylphosphate (TBP), adsorption with activated carbon, ion exchange, and precipitation methods by formic acid, hydrazine, hypophosphorous acid, and ascorbic acid [McDuffie, 1979; Sakurai and Hirokawa, 1996; AL-bazi and Chow, 1984; Myasoedova et al., 1985; Navratil, 1989; Kubota and Fukase, 1980; Lee et al., 1994]. In the case of precipitation methods by formic acid or hypophosphorous acid, some metals are coprecipitated with Pd [Kondo and Kubota, 1992]. But, Pd could be selectively precipitated by ascorbic acid [Kim et al., 1998] In this study, the precipitation characteristics of Pd by ascorbic acid were investigated from simulated radwaste solutions, which contained 1, 3, and 8 components.

EXPERIMENTAL

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The simulated radwaste solution used in this study was composed of 1 component (Pd), 3 components (Pd, Rh, Ru), and 8 components (Pd, Rh, Ru, Cs, Sr, Ni, Fe, Ba), respectively.

The number of the elements contained in real HLLW is more than 30. The recovery step of the platinum group metals is arranged after the first denitration step [Kubota and Fukase, 1980]. The chemical compositions of the simulated solution used in this study are shown in Table 1, based on the compositions of the supernatant liquor obtained after the first denitration of the estimated HLLW from the first cycle of the Purex process for pressurized water reactor (PWR) spent fuel with 28,000 MWd/MT and 5 year cooling time [Kubota and Fukase 1980]. The simulated solution was prepared by dissolving the nitrate salts of each metal such as Pd(II), Ru(IV), and Rh(III) as shown in Table 1. 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 mixed with a vortex mixer (Model Fisher type 37600) for 5 min and allowed to stand for 2 hours. The two phases were separated with a centrifuge and 1.0 μm cellulose membrane filter (Whatman). The concentrations of nitric acid and ascorbic acid used were in the

Table 1. Chemical compositions of the simulated radwaste solution

Components	Reagent used	Concentration	
		Mole/liter	ppm
Pd	Pd(NO$_3$)$_2$	0.018	1915
Rh	Rh(NO$_3$)$_3$	0.008	823
Ru	RuNO(NO$_3$)$_3$	0.034	3436
Cs	CsNO$_3$	0.0371	4929
Sr	Sr(NO$_3$)$_2$	0.0165	1445
Ni	Ni(NO$_3$)$_3$·6H$_2$O	0.006	352
Fe	Fe(NO$_3$)$_3$·9H$_2$O	0.0232	1296
Ba	Ba(NO$_3$)$_2$	0.0207	2843

ranges of 0.1-4 M and 0.01-0.14 M, respectively. The concentrations of Pd, Rh, Ru, and Ba in the sample solution were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP, Model ISA Jobin-Yvon JY 38 PLUS). The concentration of Ni, Fe, Cs and Sr was analyzed by a flame atomic absorption spectrophotometer (AAS, Perkin-Elmer, Model 3100). To investigate the form of Pd precipitate, the Pd precipitate was examined by X-ray diffractor (XRD, Model SIEMENS D5000) and a scanning electron microscope (SEM : JEOL, JSN-5200, Japan).

RESULTS AND DISCUSSION

The redox reaction between ascorbic acid (H_2A ; $C_6H_8O_6$) and dehydroascorbic acid ($A : C_6H_6O_6$) in acidic solution is expressed as follows [Creutz, 1981].

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

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 by the ascorbic acid can be precipitated
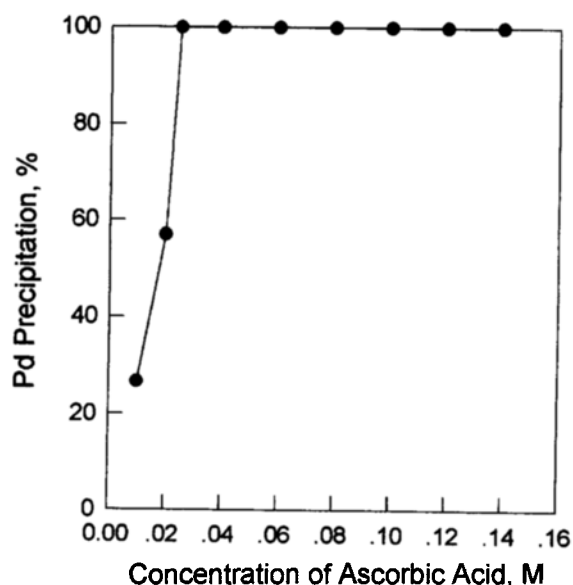
by the reduction of Pd^{+2} to the Pd metal as the following reduction reaction,

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

The precipitation characteristics of Pd in a 1 component system by ascorbic acid in 0.5 M nitric acid are shown in Fig. 1. From the results, as the ascorbic acid concentration increases, the precipitation yield of Pd increases. Pd over 99.9 % was precipitated at ascorbic acid concentrations above 0.025 M. Based on the XRD and SEM analysis results of Pd precipitate (Fig. 2 and Fig. 3), it was confirmed that Pd precipitate
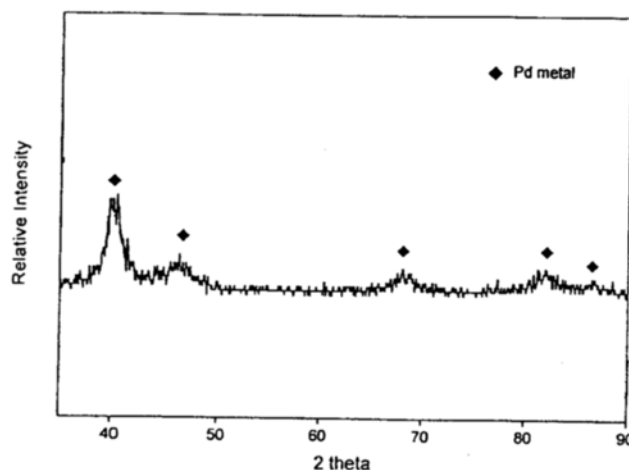

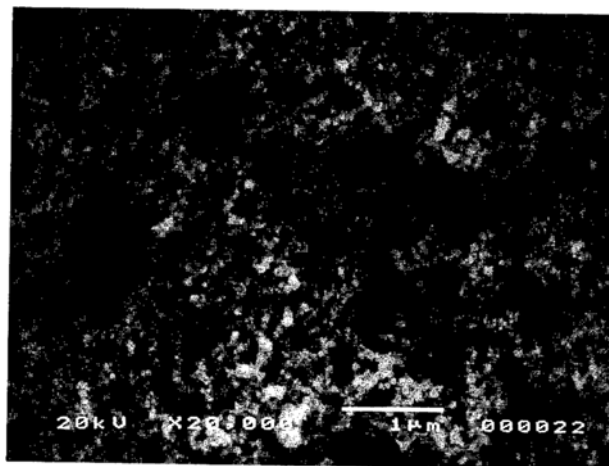Fig. 2. XRD pattern of Pd precipitate in 8 components system.

Fig. 3. SEM micrograph of Pd precipitate in 8 components system.

Fig. 1. Precipitation yield of palladium with different concentration of ascorbic acid in 1 component system [HNO₃ Con. : 0.5 M].

Table 2. Redox system of each element and reduction chemical reaction by ascorbic acid [Creutz, 1981; Lide, 1991]

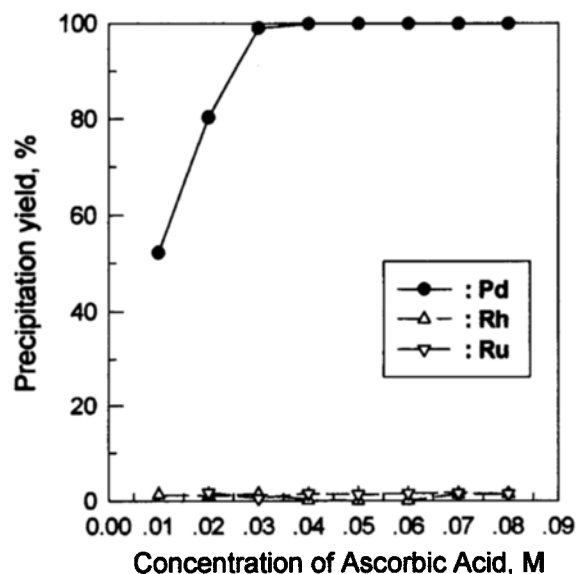| Elememts	Oxidation-reduction system	Standard potential, V	Reduction chemical reaction	Value of potential, V
Pd	$Pd^{+2}+2e \longleftrightarrow Pd(s)$	+0.951	$Pd^{+2} + H_2A \longleftrightarrow Pd(s)+A+2H^+$	+0.551
Rh	$Rh^{+3}+3e \longleftrightarrow Rh(s)$	+0.76	$2Rh^{+3} + 3H_2A \longleftrightarrow Rh(s)+3A+6H^+$	+0.34
Ru	$Ru^{+4}+e \longleftrightarrow Ru^{+3}$	+0.908	$2Ru^{+4} + H_2A \longleftrightarrow 2Ru^{+3}+A+2H^+$	+0.508
Fe	$Fe^{+3}+e \longleftrightarrow Fe^{+2}$	+0.771	$2Fe^{+3} + H_2A \longleftrightarrow 2Fe^{+2}+A+2H^+$	+0.371
Cs	$Cs^++e \longleftrightarrow Cs(s)$	-2.92	$2Cs^{+2} + H_2A \longleftrightarrow Cs(s)+A+2H^+$	-3.32
Sr	$Sr^{+2}+2e \longleftrightarrow Sr(s)$	-2.89	$Sr^{+2} + H_2A \longleftrightarrow Sr(s)+A+2H^+$	-3.41
Ni	$Ni^{+2}+2e \longleftrightarrow Ni(s)$	-0.25	$Ni^{+2} + H_2A \longleftrightarrow Ni(s)+A+2H^+$	-0.65
Ba	$Ba^{+2}+2e \longleftrightarrow Ba(s)$	-2.912	$Ba^{+2} + H_2A \longleftrightarrow Ba(s)+A+2H^+$	-3.312

Fig. 4. Precipitation yield of each element with different concentration of ascorbic acid in 3 components system [HNO₃ Con. : 0.5 M].

formed by ascorbic acid was Pd metal and was aggregated by particle less than 0.1 μm.

Fig. 4 shows the precipitation characteristics of 3 elements with ascorbic acid concentration in 0.5 M nitric acid. From the result, Pd over 99.9 % was quantitatively precipitated at ascorbic acid concentration above 0.03 M while other elements mainly remained in solution. Although Rh expected to be precipitated due to the reduction potential by ascorbic acid, 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 reducible element. Therefore, more ascorbic acid was required to obtain the same yield of Pd precipitation in a 3 component system than that in a 1 component system. The precipitation characteristics of each element with different concentration of ascorbic acid in 0.1 M, 0.5 M, and 2.0 M nitric acid are shown in Fig. 5. Pd was selectively precipitated with the increase of ascorbic acid concentration, while other elements were scarcely precipitated. Pd over 99.5 % was precipitated at ascorbic acid concentration above 0.04 M when the nitric acid concentration was below 0.5 M. In addition, the ascorbic acid concentration required for the complete reduction of elements increased because of reducible metals such as Ru, Rh, and Fe. As the concentration of ascorbic acid increased, the precipitation yield of Pd increased. In the case of 2.0 M nitric acid concentration, Pd over 99.5 % was precipitated at ascorbic acid concentration above 0.06 M.

Fig. 6 shows the dependency of the precipitation yield of Pd on nitric acid concentration for the 8 component 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^-) [Lide, 1991], it is likely that nitrate ion (NO_3^-) in nitric acid solu-
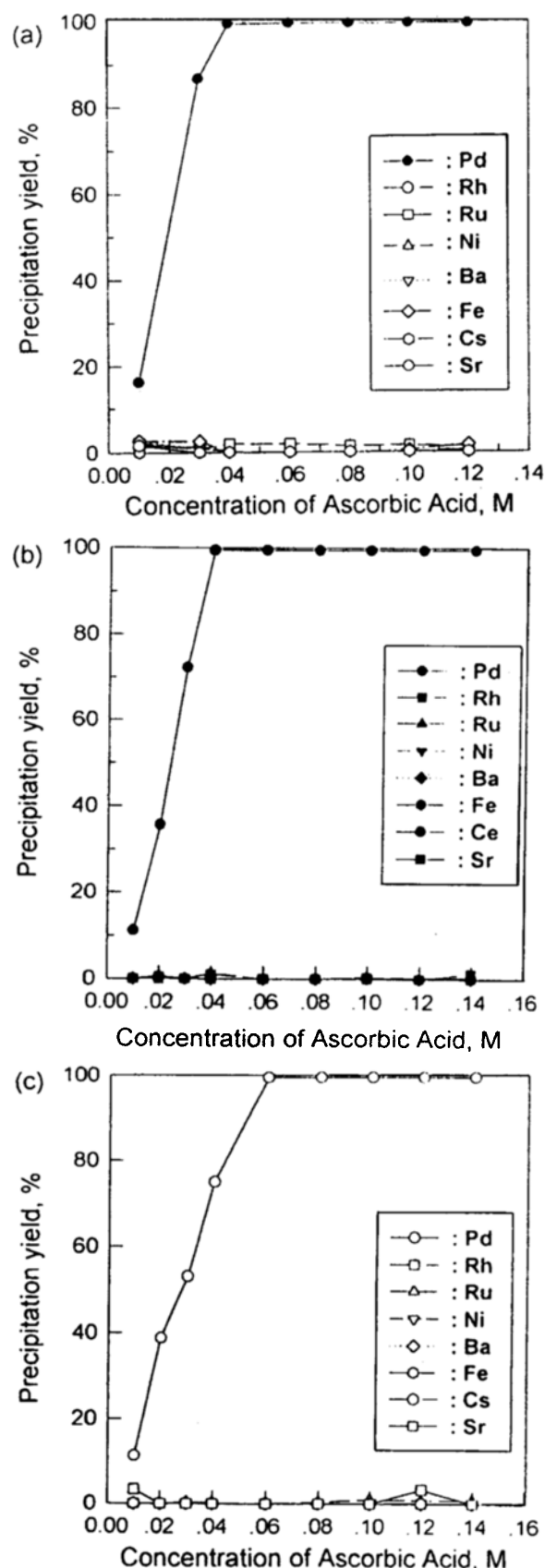
Fig. 5. Precipitation yield of each element with different concentration of ascorbic acid in 8 components system. (a) HNO₃ Con. : 0.1 M, (b) HNO₃ Con. : 0.5 M, (c) HNO₃ Con. : 2.0 M
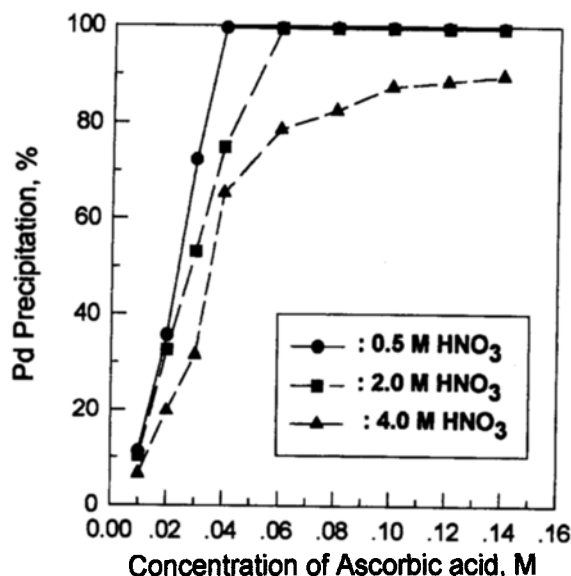
Fig. 6. Effect of nitric acid concentration on Pd precipitation with different concentration of ascorbic acid in 8 components system.

tion may be reduced to nitro (NO_2^-) ion or nitrosyl (NO^-) ion by the ascorbic acid. Therefore, as the nitric acid concentration increases, the yield of Pd precipitation decreases. In addition, a greater quantity of ascorbic acid was required for complete reduction of elements.

CONCLUSIONS

The precipitation characteristics of Pd by ascorbic acid were investigated. Pd was selectively precipitated by the ascorbic acid. Pd over 99.9 % in the 1 and 3 component systems in 0.5 M nitric acid was quantitatively precipitated at a concentration of ascorbic acid above 0.025 M and 0.03 M, respectively. In addition, when the nitric acid concentration in the 8 component system was below 2.0 M, Pd over 99.5 % was selectively precipitated at ascorbic acid concentration above 0.06 M while other elements mainly remained in solution. As the nitric acid concentration in the simulated solution increased, the precipitation yields of Pd decreased, and the concentration of ascorbic acid required for complete reduction of elements increased. It is assumed that Pd precipitate may have a high purity over 99 % because Pd is selectively precipitated by ascorbic acid from the simulated radwaste solution.

Based on these experimental results, Pd can be easily and selectively separated from a simulated radwaste solution by ascorbic acid. It is estimated that the Pd precipitate can be used for industrial purposes such as the manufacture of Pd catalyst.

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