J. Min. Metall. Sect. B-Metall. 58 (2) (2022) 311 - 319

Journal of Mining and Metallurgy, Section B: Metallurgy

SELECTIVE PRECIPITATION OF AMMONIUM HEXACHLOROPALLADATE FROM LEACHING SOLUTIONS OF CEMENTED PALLADIUM WITH ZINC

V.N.H. Nguyen, S.J. Song, M.S. Lee *

Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Republic of Korea

(Received 08 February 2022; Accepted 26 June 2022)

Abstract

Palladium (Pd) present in spent electroplating solutions is concentrated by cementation with zinc (Zn) metal powder. Therefore, it is necessary to recover Pd from the cemented Pd. In this work, recovery of pure Pd(IV) compounds from the leaching solutions of the cemented Pd was investigated by using selective precipitation method. It was found that the existence of Pd(IV) in the aqueous solutions is critical for the precipitation with NH_4Cl*. Precipitation experiments of Pd(IV) from the synthetic aqua regia solution containing Pd(IV) and Zn(II) was tested. Afterwards, the optimum precipitation conditions were applied to recover Pd(IV) precipitates from the real* H_2SO_4 *and HCl leaching solutions containing NaClO as an oxidizing agent. The selective precipitation resulted in the recovery of extra pure* $(NH_4)_2PdCl_6$ *from real leaching solutions under the conditions of 1:30 molar ratio of Pd(IV) to* NH_4Cl *at 60°C within 30 min. The precipitation percentage of Pd(IV) from the* H_2SO_4 *and HCl solutions was over 99.9 and 98.2%, respectively. A simple hydrometallurgical process consisting of cementation, leaching, and precipitation was proposed for the recovery of pure Pd(IV) compounds from spent electroplating solution.*

Keywords: *Precipitation; Cemented Pd; Ammonium hexachloropalladate; Spent electroplating solution; Recovery*

1. Introduction

Palladium is an important element for the production of electronic materials, catalysts in chemistry or automobile vehicle industry [1-4]. In practice, electroplating of palladium (Pd) is practiced in the manufacture of electronic devices [1]. The spent electroplating solutions contain a small amount of Pd which can be concentrated by cementation with zinc metal powder. Considering the increase in demand for Pd metal or compounds, it is necessary to recover Pd present in the cemented Pd [5].

To recover pure metals or compounds from the secondary resources, hydrometallurgical processes are employed. In hydrometallurgical process, the target elements present in the secondary resources are dissolved by either inorganic or organic acid solutions. Since the leaching solutions contain not only the target metal ions but also some impure elements, these impure elements should be separated from the leaching solution by employing some unit operations like solvent extraction, ion exchange and precipitation [6-8]. In developing a process, it is necessary to find one which can meet both recovery efficiency and the minimization of environmental burden. When precipitation can be employed as a final step to recover pure compound from the leaching solution without any separation steps, the process would have lots of advantages in terms of process efficiency and environmental burden.

Most of the reported processes for the recovery of either Pd metal or compounds from aqueous solutions can be classified into reduction and precipitation from purified solution. Some conditions have been reported to precipitate Pd ions from several kinds of aqueous solutions containing other ions. It has been found that addition of $NaClO_3$ to the acidic solution in the absence of platinum ion could oxidize Pd(II) to Pd(IV) and slowly precipitate Pd(IV) as $(NH_4)_2PdCl_6$ at high temperature (90°C) [9,10]. Besides, $(NH_4)_2PdCl_6$ can be precipitated from the aqua regia solution containing Zn, Ni, Ag, and Au by adding NH_4Cl but the purity of the precipitates has not been reported [11]. Since Pd ion has a higher reduction potential, Pd metal can be recovered by using $NaBH_4$ as a reducing agent from the leaching solution of multilayer ceramic capacitors, waste printed circuit boards and spent activated carbon-supported palladium catalysts. However, these processes have several disadvantages, such as the decomposition of

---

* *Corresponding author: mslee@mokpo.ac.kr*

https://doi.org/10.2298/JMMB220208013N

$NaBH_4$ to H_2 in acidic solution, the low recovery efficiency, lower purity of Pd metal, and requirement of high temperature (100ºC) [12,13]. In similar way, both Pd and Au can be precipitated by adding $NaBH_4$ to hydrochloric acid leaching solution, but the separation of the two metals is necessary [14]. In addition, ascorbic acid can reduce Pd together with Rh and Re from 0.5 M HNO_3 solution, but subsequent separation steps are necessary to recover pure Pd from the reduced metallic alloys [15]. Moreover, hydrazine can reduce Pd from weak hydrochloric acid solution [16]. Compared to precipitation process, the acidity of the solution is of immense importance to recover Pd metal by reduction with reducing agents.

In our previous work, hydrometallurgical processes consisting of leaching followed by solvent extraction were reported to recover Pd from the cemented Pd. In these processes, Pd ions were separated over Zn(II) from the leaching solutions of the cemented Pd by solvent extraction with commercial extractants and ionic liquids [7, 17]. The purpose of present study was to investigate a hydrometallurgical process to recover pure Pd compounds from leaching solution of the cemented Pd without employing solvent extraction steps. For this purpose, precipitation of Pd(IV) compound from the H_2SO_4 and HCl leaching solutions of cemented Pd was investigated. Moreover, selective precipitation of pure Pd compound from the synthetic aqua regia solution was also tried. First, the synthetic solution containing Pd(IV) and Zn(II) was tested for selective precipitation of Pd(IV). Subsequently, the optimum conditions were applied to the recovery of Pd(IV) precipitates from the real H_2SO_4 and HCl leaching solutions of cemented Pd. Precipitation conditions such as the molar ratio of precipitant to metal ion, reaction time and temperature, and HCl concentration were optimized. The characteristics of $(NH_4)_2PdCl_6$ precipitates was analyzed by X-ray diffractometer and high-resolution scanning electron microscopy measurement. From the obtained results, a simple hydrometallurgical process was proposed for the recovery of pure Pd compound from the cemented Pd.

2. Experimental

2.1. Reagents and chemicals

The synthetic leaching solution containing Pd(IV) and Zn(II) was prepared by dissolving $PdCl_4$ (Alfa Aesar, Ward Hill, MA, USA, 99.9%) and $ZnCl_2$ (Duksan Co., Gyungki-do, Korea, 99%) in 75% aqua regia solution. The concentration of Pd(IV) and Zn(II) in the synthetic aqua regia solution was controlled to 2000 mg/L and 40 mg/L, respectively. Concentrated hydrochloric acid (HCl, Daejung Chemical. Co., Shiheung, Korea, 35%) and HNO_3 (Daejung Co., Shiheung, Korea, 60%) with volume ratio of 3:1 was prepared as aqua regia solution which was diluted to 75% with distilled water. Hydrogen peroxide (Daejung Chemical. Co., Shiheung, Korea, >30%), NaClO solution (Sigma-Aldrich Co., with available chlorine 10–15%, USA) were used as oxidizing agents. HCl and H_2SO_4 (Daejung Co., Shiheung, Korea, 95%) solutions were used as leaching agents and NH_4Cl (Duksan Co., Gyungki-do, Korea, 99%) was added as a precipitant and all the employed chemicals were of analytical grade.

2.2. Experimental procedure and analytical methods

The precipitation of Pd(IV) from synthetic solutions and real leaching solutions was performed by adding NH_4Cl to the aqueous solution in a beaker. The reaction mixtures were stirred by a magnetic stirrer in a heating mantle to control the temperature, time, and stirring speed. After the required period, the reaction mixtures were left to stand for 30 min. Precipitates were collected, and then dried in an oven (Wiseven Wids, Daihan Scientific Co., Korea) at 60°C for 12 hours. X-ray diffractometer (XRD, X'Pert-PRO, the Netherlands) and analytical high-resolution scanning electron microscopy (HR-SEM, SU-70, Hitachi, Japan) were used to verify the characteristics of the precipitates. The purity of the precipitates was confirmed by dissolving them in 5% NH_3 solution and then the concentration of the metal ions was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos, Cleve, Germany). The concentration of hydrogen ions in solutions was measured by volumetric titration method. First, the solutions were diluted 10 times with distilled water and the concentration of hydrogen ions in the resulting solutions was measured by titration with 0.5 M Na_2CO_3 standard solution according to Vogel's method [18]. The precipitation percentage (X%) of Pd(IV) was calculated as:

$$X\% = \left(\left(M_i - M\right)/M_i\right)\times 100 \qquad (1)$$

where M_i and M are the mass of metal ions in the aqueous phase before and after the precipitation, respectively.

In the precipitation experiments, the effect of some variables such as the molar ratio of precipitant to the metal ion, reaction time and temperature on the precipitation of the metal ions was investigated. In addition, the effect of HCl concentration in the real leaching solutions on the precipitation of Pd(IV) was also studied. Experiments were done two times with errors within ± 5%.

3. Results and discussion

3.1. Precipitation of Pd(IV) from synthetic aqua regia solution

3.1.1. Effect of molar ratio of Pd to NH_4Cl on precipitation of Pd(IV) from the synthetic aqua regia solution

In precipitation, the molar ratio of the reactants is one of the most important variables. To investigate this effect on the precipitation of Pd(IV), the molar ratio of Pd(IV) to NH_4Cl was varied from 1:5 to 1:40 and Figure 1 shows the results. First, the synthetic solution of 75% aqua regia containing 2000 mg/L Pd(IV) and 40 mg/L Zn(II) was tested. The existence of Pd(IV) as $PdCl_6^{2-}$ in the solution is related to the strong oxidizing property of aqua regia [19-22]. Reactions were run at 60°C within 180 min. Figure 1 shows that precipitation percentage of Pd(IV) increased from zero to 99.95% when molar ratio of Pd(IV) to NH_4Cl increased from 1:5 to 1:30 and then constant with the further increase of the molar ratio. Zn(II) was not precipitated in these experimental conditions. Zn(II) has a strong tendency to form complex with chloride ions like $ZnCl_4^{2-}$ [23], which can react with NH_4^+ ion to form a soluble ammonium salt in solution [24]. The purity of Pd(IV) precipitate was over 99.99%. The precipitation reaction of Pd(IV) by NH_4Cl can be represented as

$$PdCl_6^{2-}{}_{(a)} + 2NH_4^+{}_{(a)} = \left(NH_4\right)_2 PdCl_{6(s)} \quad (2)$$

where subscript a and s represent aqueous and solid, respectively.

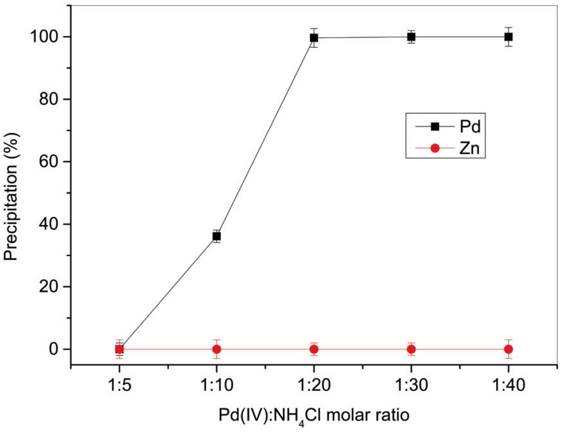

Figure 1. *Effect of molar ratio of Pd(IV) to NH_4Cl on precipitation of Pd(IV). Conditions: solution: 2000 mg/L Pd(IV) and 40 mg/L Zn(II); Molar ratio of Pd(IV) to NH_4Cl = 1:5-1:40; 180 min; 60°C; 500 rpm*

3.1.2. Effect of temperature and time on precipitation of Pd(IV) from the synthetic aqua regia solution

In these experiments, the molar ratio of Pd(IV) to NH_4Cl was fixed at 1:30 and reactions were run for 180 min. To investigate the influence of temperature on the precipitation of Pd(IV), precipitation experiments were performed in the range of 25 - 60°C and the data is shown in Figure 2. The results showed that the quantitative precipitation of Pd(IV) with NH_4Cl was obtained at 25°C and temperature effect was negligible. The precipitation percentage of $(NH_4)_2PdCl_6$ was around 99.95% in the studied temperature range.

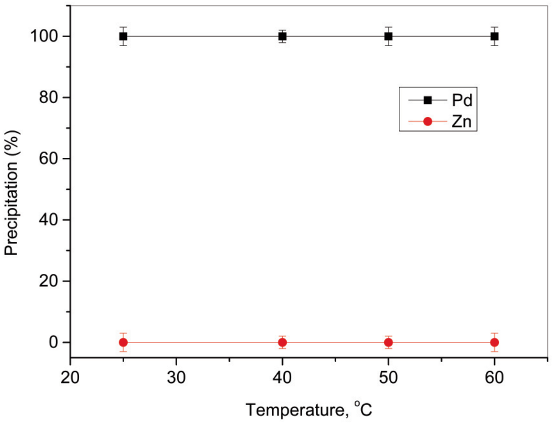

Figure 2. *Effect of temperature on precipitation of $(NH_4)_2PdCl_6$. Conditions: solution: 2000 mg/L Pd(IV) and 40 mg/L Zn(II); Molar ratio of Pd(IV) to NH_4Cl: 1:30; 180 min; 25-60°C; 500 rpm*

The effect of reaction time on the precipitation of Pd(IV) from the synthetic solution was investigated from 30 to 180 min. Molar ratio of Pd(IV) to NH_4Cl was fixed at 1:30 and experiments were done at 25°C. Figure 3 shows that the reaction time negligibly affected the precipitation percentage of Pd(IV) as reaction time increased from 30 to 180 min. These results indicated that the precipitation reaction of

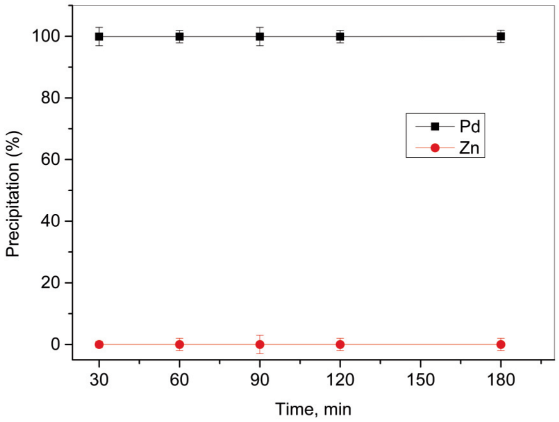

Figure 3. *Effect of time on precipitation of Pd(IV). Conditions: solution: 2000 mg/L Pd(IV) and 40 mg/L Zn(II); Molar ratio of Pd(IV) to NH_4Cl = 1:30; 30-180 min; 25°C; 500 rpm*

Pd(IV) with NH_4Cl is fast and complete precipitation can be achieved within 30 min.

From the obtained results, the optimum condition for the precipitation of Pd(IV) from the synthetic solution by NH_4Cl was 1:30 molar ratio of Pd(IV) to NH_4Cl within 30 min at room temperature. Under the optimum conditions, the precipitation percentage of Pd(IV) from the synthetic solution was 99.95% and the purity of the precipitate was over 99.99%. Zn(II) was not precipitated at all in this condition. Therefore, it can be said that the Pd(IV) was selectively precipitated over Zn(II) from the aqua regia solution.

3.2. Precipitation of Pd(IV) compound from real leaching solution

3.2.1. From real H_2SO_4 leaching solution

Our previous work indicated that the complete leaching of the Pd and Zn in cemented Pd was obtained by employing either HCl or H_2SO_4 solution containing H_2O_2 or NaClO as an oxidizing agent for 60 min from 25 to 60°C (see Table 1) [6]. Based on these conditions, leaching solutions of the cemented Pd were prepared and the concentrations of Pd(IV) and Zn(II) in the real leaching solution were 1926 mg/L and 74 mg/L, respectively. The results in the previous section indicated that Pd(IV) can be selectively precipitated over Zn(II) by using NH_4Cl as a precipitant. Therefore, NH_4Cl would be appropriate to selectively precipitate Pd(IV) from real leaching solutions of the cemented Pd.

Table 1. *Leaching conditions for mixture of Pd and Zn metals (pulp density: 2g/L) [6]*

Acidic media	Concentration, M	Oxidizing agent	Temperature, °C	Time, min
HCl	7	0.5 % H_2O_2	60	60
	5	1% NaClO	25	60
H_2SO_4	5	1.5% NaClO	25	60

First, the optimum condition for the precipitation of Pd(IV) from the synthetic solution by NH_4Cl was applied to real H_2SO_4 leaching solution. When the molar ratio of Pd(IV) to NH_4Cl was 1:30, the precipitation percentage of Pd(IV) from the real leaching solution at 25°C was only 52.5% and thus the experiments were done at 60°C to enhance the precipitation of Pd(IV). Moreover, the molar ratio of Pd(IV) to NH_4Cl was also varied from 1:5 to 1:40 to investigate this effect from real H_2SO_4 leaching solution and the obtained results are shown in Figure 4. The precipitation percentage of Pd(IV) increased from 49.5 to 99.98% when molar ratio of Pd(IV) to NH_4Cl increased from 1:5 to 1:30 and then constant with the further increase of the molar ratio. Zn(II) was not precipitated in these experimental conditions. The purity of Pd(IV) compound was over 99.99% and its chemical formula was verified by the XRD analysis to be ammonium hexachloropalladate ($(NH_4)_2PdCl_6$) with red color. This result indicates that it is possible to recover $(NH_4)_2PdCl_6$ with high purity from the leaching solutions containing Pd(IV) and Zn(II) by one step precipitation with NH_4Cl. Considering the relevant steps involved in the multi-stage extraction and stripping of Pd(II) over Zn(II), this precipitation process has several advantages in real operation. The morphology of $(NH_4)_2PdCl_6$ was also obtained by SEM analysis (see Figure 5). As is seen in Figure 5b, the morphology of the precipitates was uniform. This revealed that the recovery of pure Pd(IV) compound from the real 5 M H_2SO_4 leaching solution was achieved with high performance.

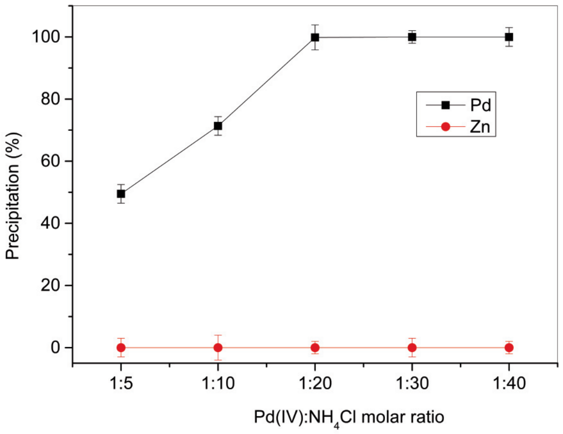

Figure 4. *Effect of molar ratio of Pd(IV) to NH_4Cl on precipitation of $(NH_4)_2PdCl_6$ from H_2SO_4 real leaching solution. Conditions: solution: 1926 mg/L Pd(IV) and 74 mg/L Zn(II); Molar ratio, Pd(IV):NH_4Cl = 1:5-1:40; 30 min; 60°C; 500 rpm*

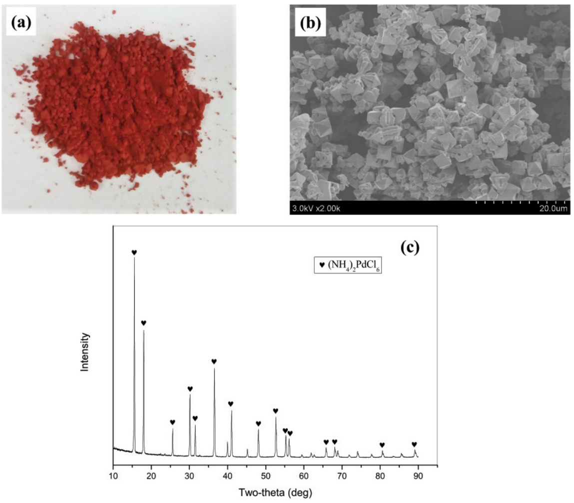

Figure 5. *Powders (a), SEM images (b), and XRD pattern (c) of $(NH_4)_2PdCl_6$ precipitates from real 5 M H_2SO_4 leaching solution*

3.2.2. From real HCl leaching solution

3.2.2.1. Effect of HCl concentration in real leaching solution on the precipitation of Pd(IV)

The precipitation of Pd(IV) from the real 5 M HCl leaching solutions containing 1% NaClO was also tested. Reaction was done at 60°C for 30 min and the molar ratio of Pd(IV) to NH_4Cl was controlled to 1:30. The results indicated that 78.9% of Pd(IV) was precipitated in these experimental conditions. To investigate the influence of HCl concentration on precipitation of Pd(IV) from real HCl leaching solution, the HCl concentration was varied from 1 to 7 M. For this purpose, the real leaching solution of 7 M HCl and 1% NaClO was prepared at 25°C within 60 min, and then NaOH was added to adjust the HCl concentration of the leaching solution from 1 to 5 M. Subsequently, the precipitation of Pd (IV) with NH_4Cl was done under the conditions of molar ratio of Pd(IV) to NH_4Cl: 1:30; 30 min, 500 rpm, 60°C. The results in Figure 6 showed that precipitation percentage of Pd(IV) increased from 0.7 to 98.2% when HCl concentration increased from 1 to 7 M. This revealed that the acidity of solution has a significant effect on precipitation efficiency. When NH_4Cl is dissolved in an aqueous solution, the concentration of NH_4^+ depends on the solution acidity owing to its dissociation into ammonia and proton. Since ammonium ion is a weak acid, its dissociation would be suppressed as the acidity of the solution becomes stronger, which can be represented as

$$NH_4^+{}_{(a)} + H_2O_{(a)} = NH_{3(a)} + H_3O^+{}_{(a)} \qquad (3)$$

Therefore, it can be thought that the dissociation of ammonium ion would be suppressed when the concentration of HCl is higher than 5 M and thus insoluble $(NH_4)_2PdCl_6$ can be precipitated.

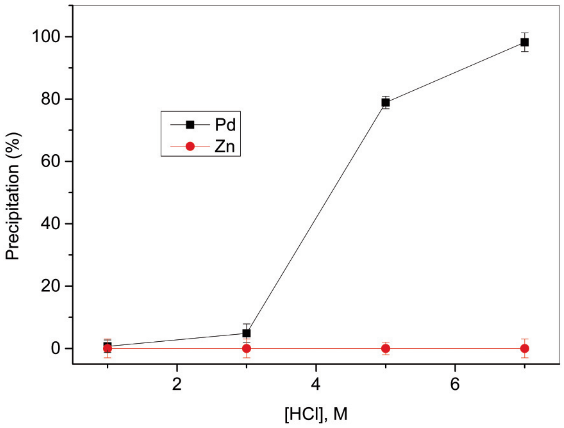

Figure 6. *Effect of HCl concentration on precipitation of Pd(IV) from 7 M HCl and 1% NaClO real leaching solution. Conditions: solution: 1926 mg/L Pd(IV) and 74 mg/L Zn(II); Molar ratio, Pd(IV):NH_4Cl = 1:30; 30 min; 60°C; 500 rpm*

3.2.2.2. Effect of molar ratio of Pd(IV) to NH_4Cl on precipitation of Pd(IV) from real HCl leaching solution

Owing to the efficient precipitation of Pd(IV) from the real leaching solution of 7 M HCl and 1% NaClO, the precipitation at this condition was studied further. To investigate the effect of molar ratio of Pd to NH_4Cl on the precipitation, this parameter was changed from 1:5 to 1:40 and the results are shown in Figure 7. The precipitation percentage of Pd(IV) from 7 M real HCl containing 1% NaClO increased from 43.99 to 98.2% when molar ratio of Pd(IV) to NH_4Cl increased from 1:5 to 1:30 and then constant with the further increase of molar ratio (see Figure 7). Zn(II) was not precipitated in these experimental conditions. Figure 8 illustrates the chemical formula and morphology of $(NH_4)_2PdCl_6$ precipitates which were confirmed by XRD and SEM measurements. The clear XRD patterns of the precipitate indicate that the purity of $(NH_4)_2PdCl_6$ precipitates would be very high. In order to determine the purity of the precipitates, the precipitates were first dissolved into 5% NH_3 solution and the purity was found to be higher than 99.99%. Moreover, SEM images show that there are some fluctuations in the particle size and shape of the precipitates. These results confirm that it is possible to recover pure Pd(IV) compound from the real 7 M HCl leaching solution containing Zn(II) by adding NH_4Cl as a precipitant.

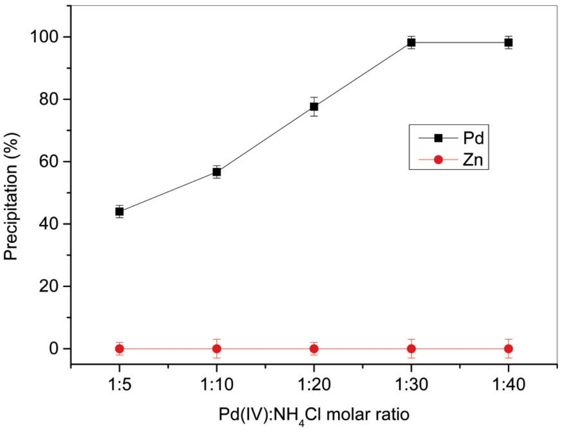

Figure 7. *Effect of molar ratio of Pd(IV) to NH_4Cl on precipitation of Pd from 7 M HCl real leaching solution containing 1% NaClO. Conditions: solution: 1926 mg/L Pd(IV) and 74 mg/L Zn(II); Molar ratio, Pd(IV):NH_4Cl = 1:5-1:40; 30 min; 60°C; 500 rpm*

Besides, the precipitation of Pd ions from the real 7 M HCl leaching solutions containing 0.5% H_2O_2 as an oxidizing agent was also tested. Reactions were done at 60°C for 30 min by varying the molar ratio of Pd(IV) to NH_4Cl from 1:5 to 1:40. The results indicated that no precipitate was formed in these experimental conditions. This might be related to the existence of Pd(II) in the leaching solution of 7 M HCl containing 0.5% H_2O_2. This agreed well with previous reports on the formation of $PdCl_4^{2-}$ as dominant species of Pd(II) in the HCl leaching solution when H_2O_2 was employed as an oxidizing agent [9,10,20,25].

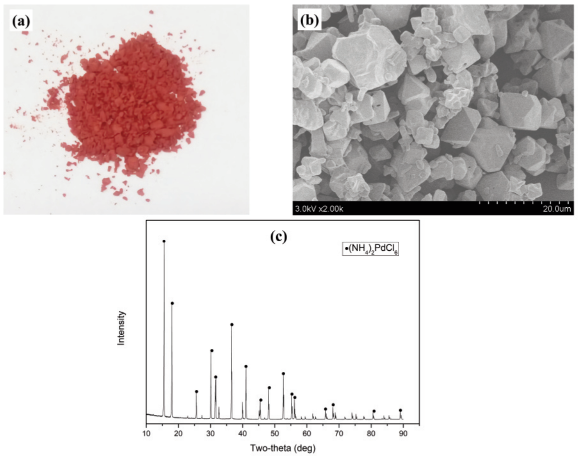

Figure 8. *Powders (a), SEM images (b), and XRD pattern(c) of* $(NH_4)_2PdCl_6$ *precipitates from real 7 M HCl and 1% NaClO solution*

Pd is a noble metal and thus use of an oxidizing agent is necessary to dissolve by using inorganic acid solutions such as HCl and H_2SO_4. There are two kinds of Pd ions in aqueous solution, namely Pd(II) and Pd(IV). Figure 9 shows the Eh-pH diagram of Pd-Cl-H_2O system at 25°C [26]. This diagram indicates that very strong oxidizing conditions are necessary to dissolve Pd metal as $PdCl_6^{2-}$ by using HCl solution containing oxidizing agent. Moreover, the stable region of $PdCl_6^{2-}$ is much smaller than that of $PdCl_4^{2-}$. Table 2 lists the reduction potential values of Pd(II), Pd(IV), H_2O_2 and NaClO [24,26]. The values listed in Table 2 indicate that the oxidation potential of Pd metal to $PdCl_4^{2-}$(-0.591 V) is much higher than that to $PdCl_6^{2-}$(-0.96 V). It can be said from thermodynamic point of view that Pd metal would be dissolved as $PdCl_4^{2-}$ during the leaching with HCl solution containing either H_2O_2 or NaClO because it would result in larger Gibbs free energy change [9]. Moreover, kinetic stability is as important as thermodynamic stability in considering the reaction product. It is known that Pd(II) is more kinetically stable than Pd(IV) in HCl solutions [27]. Therefore, Pd metal would be dissolved as Pd(II) during the leaching with HCl solution containing H_2O_2 or NaClO as an oxidizing agent.

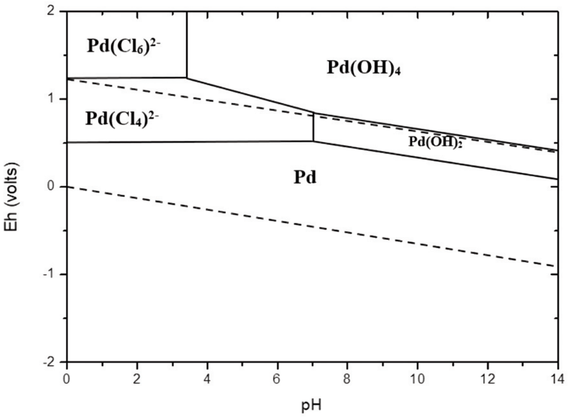

Figure 9. *Eh-pH diagram of Pd-Cl-*H_2O *system at 25°C*

Table 2. *Standard reduction potentials of some reactions at 25°C [24,26]*

Reaction	E°(V)
$PdCl_4^{2-} + 2e = Pd + 4Cl^-$	0.591
$PdCl_6^{2-} + 4e = Pd + 6Cl^-$	0.96
$H_2O_2 + 2H^+ + 2e = 2H_2O$	1.763
$Cl_2 + 2e = 2Cl^-$	1.36
$2ClO^- + 2H^+ + e = 0.5Cl_2 + H_2O$	0.83
$ClO^- + 2H^+ + 2e = Cl^- + H_2O$	1.715

There is some difference in chemical properties between Pd(II) and Pd(IV). Pd(II) is a soft acid but Pd(IV) is harder than Pd(II) on the basis of hard soft acid base principle owing to the larger charge density of Pd(IV) than that of Pd(II). Since NH_3 is a hard base, Pd(IV) has a strong tendency to form coordinate bond with NH_4^+ than with Pd(II). This is well illustrated in the solubility data that $(NH_4)_2PdCl_6$ is insoluble in water whereas $(NH_4)_2PdCl_4$ is soluble [8, 10, 24]. Therefore, it can be said that the existence of Pd ions as $PdCl_6^{2-}$ is necessary to apply the precipitation method from HCl solution by employing NH_4Cl.

In order to recover Pd as $(NH_4)_2PdCl_6$ precipitates from the real HCl leaching solution containing H_2O_2, addition of a strong oxidizing agent like $NaClO_3$ to the leaching solution is necessary to oxidize Pd(II) to Pd(IV) and thus to promote the precipitation [9, 10]. Instead of adding $NaClO_3$, NaClO was added to the HCl solution during leaching process as an oxidizing agent in this work. Extra pure ammonium hexachloropalladate ($(NH_4)_2PdCl_6$) was recovered by adding NH_4Cl to the real leaching solution of HCl containing NaClO as an oxidizing agent. Our results indicated that either HCl or H_2SO_4 leaching solution can be employed as a leaching agent for the cemented Pd and NaClO should be added as an oxidizing agent. The role of NaClO is to enhance the formation of $PdCl_6^{2-}$ which can be precipitated by NH_4Cl. The formation of $PdCl_6^{2-}$ can be represented as Eqs. (4)-(6)[9].

$$NaClO_{(a)} + 2HCl_{(a)} = NaCl_{(a)} + Cl_{2(gas)} + H_2O_{(a)} \quad (4)$$

$$Cl_{2(gas)} + 2e = 2Cl^{-}_{(a)} \quad (5)$$

$$PdCl_4^{2-}{}_{(a)} + 2Cl^{-}_{(a)} = PdCl_6^{2-}{}_{(a)} + 2e \quad (6)$$

Moreover, precipitation efficiency greatly depended on the concentration of hydrogen ions in the HCl real leaching. Therefore, control of HCl concentration in real leaching solutions is important to obtain high precipitation performance. The advantages of the present work lie in the selective precipitation of Pd(IV) in one step and the purity of Pd(IV) compound is so high (>99.9%). Compared to the leaching followed by solvent extraction, this method is more economic because it reduces the number of separation steps involving extraction and stripping of Pd(II) from the loaded organic phase (Cyanex 301) by aqua regia solution [17]. Therefore, the amount of chemicals and thus the waste water can be reduced. Moreover, the precipitation performance was high and complete recovery of extra pure Pd(IV) compound would be possible. Therefore, a simple hydrometallurgical process can be commercially developed for the recovery of pure Pd(IV) from spent electroplating solutions containing a small amount of Pd(II).

4. Conclusions

A process for the recovery of pure Pd(IV) compound from spent electroplating solutions containing a small amount of Pd(II) was investigated. The process consisted of cementation of Pd ions with zinc metal, leaching of the cemented Pd and then selective precipitation of the dissolved Pd ions. First, the selective precipitation of Pd(IV) over Zn(II) with NH_4Cl as a precipitant from synthetic aqua regia solution was tested. Subsequently, optimum conditions from these experiments were applied to recover pure Pd(IV) compound from the real leaching solutions of the cemented Pd by either H_2SO_4 or HCl in the presence of NaClO as an oxidizing agent. The precipitation of Pd(IV) as ammonium hexachloropalladate ($(NH_4)_2PdCl_6$) from real leaching solutions was achieved under the conditions of 1:30 molar ratio of Pd(IV) to NH_4Cl in 30 min at 60ºC. The precipitation percentage of Pd(IV) from real H_2SO_4 leachate was higher than 99.98%, while that was 98.2% from real HCl leachate and the purity of the precipitates was higher than 99.9%. Our results indicated that the existence of Pd(IV) in the solution is the most important in the recovery of $(NH_4)_2PdCl_6$ from the cemented Pd. Since Pd(II) cannot be precipitated with NH_4Cl, it is necessary to oxidize Pd(II) to Pd(IV) in order to apply the precipitation method. Therefore, NaClO was recommended as an oxidizing agent to dissolve Pd metal as Pd(IV). The molar ratio of Pd(IV) to NH_4Cl and control of HCl concentration are also important for the precipitation efficiency of Pd(IV). The present work is more efficient than the leaching followed by solvent extraction on the basis of recovery possibility, economics and environmental issues. From the obtained results, a simple hydrometallurgical process consisting of cementation, leaching and selective precipitation was proposed for the recovery of pure Pd(IV) compounds from spent electroplating solution.

Acknowledgments

This work was supported by the Technology Innovation Program (Development of Material Component Technology) (Project number: 20013071) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

Author Contributions

Methodology and editing: Man Seung Lee; data support: Si Jeong Song; writing-original draft preparation: Viet Nhan Hoa Nguyen. All authors have read and agreed to the published version of the manuscript.

Data availability

The data of this work could be obtained by contacting with the corresponding author by e-mail.

Declarations of competing interest

The authors declare no conflict of interest.

References

[1] M. Antler, The application of palladium in electronic connectors continuing studies result in growing use, Platinum Metals Review, 26 (3) (1982) 106-117.

[2] J. Kašpar, P. Fornasiero, N. Hickey, Automotive catalytic converters: current status and some perspectives, Catalysis Today 77 (4) (2003) 419−449. https://doi.org/10.1016/S0920-5861(02)00384-X

[3] E. Alonso, F.R. Field, R.E. Kirchain, Platinum availability for future automotive technologies, Environmental Science and Technology, 46 (23) (2012) 12986−12993. https://doi.org/10.1021/es301110e

[4] A. Khaliq, M. Rhamdhani, G. Brooks, S. Masood, Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective, Resources, 3(1) (2014) 152−179. https://doi.org/10.3390/resources3010152

[5] H.U. Sverdrup, K.V. Ragnarsdottir, A system dynamics model for platinum group metal supply, market price, depletion of extractable amounts, ore grade, recycling and stocks-in-use, Resources, Conservation & Recycling 114 (2016) 130–152. https://doi.org/10.1016/j.resconrec.2016.07.011

[6] S.J. Song, V.N.H Nguyen, M.S. Lee, Leaching of the mixture of palladium and zinc metal by hydrochloric and sulfuric acid solutions, Korean Journal of Metals and Materials, 59 (7) (2021) 469-475. https://doi.org/10.3365/KJMM.2021.59.7.469

[7] V.N.H Nguyen, S.J. Song, M.S. Lee, Recovery of pure Pd(II) from spent electroplating solutions by solvent extraction with ionic liquids from sulfuric acid leaching solution of cemented Pd, Metals, 11(8) (2021) 1320. https://doi.org/10.3390/met11081320

[8] G. Schreier, C. Edtmaier, Separation of Ir, Pd and Rh from secondary Pt scrap by precipitation and calcination, Hydrometallurgy, 68 (1-3) (2003) 69-75. https://doi.org/10.1016/S0304-386X(02)00194-9

[9] S. Ilyas, R.R. Srivastava, H. Kim, H.A. Cheema, Hydrometallurgical recycling of palladium and platinum from exhausted diesel oxidation catalysts, Separation and Purification Technology, 248 (2020) 117029. https://doi.org/10.1016/j.seppur.2020.117029

[10] A.M. Yousif, Recovery and then individual separation of Platinum, Palladium, and Rhodium from spent car catalytic converters using hydrometallurgical technique followed by successive precipitation methods, Journal of Chemistry, 2019 (2019) 1–7. https://doi.org/10.1155/2019/2318157

[11] Y.J. Park, D.J. Fray, Recovery of high purity precious metals from printed circuit boards, Journal of Hazardous Materials, 164 (2-3) (2009) 1152–1158. https://doi.org/10.1016/j.jhazmat.2008.09.043.

[12] D. Fontana, M. Pietrantonio, S. Pucciarmati, GN. Torelli, C. Bonomi, F. Masi, Palladium recovery from monolithic ceramic capacitors by leaching, solvent extraction and reduction, Journal of Material Cycles and Waste Management, 20 (2018) 1199–1206. https://doi.org/10.1007/s10163-017-0684-3

[13] Ş. Sarioğlan, Recovery of Palladium from Spent Activated carbon-supported palladium catalysts, Platinum Metals Review, 57(4) (2013) 289–296. https://doi.org/10.1595/147106713x663988

[14] A. Behnamfard, M.M. Salarirad, F. Veglio, Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation, Waste Management, 33 (11) (2013) 2354–2363. https://doi.org/10.1016/j.wasman.2013.07.017

[15] J.K. Moon, Y.J. Han, E.H. Lee, H.B. Yang, J.G. Lim, C.H. Jung, Precipitation behaviors of palladium, rhodium and rhenium with ascorbic acid, Proceedings of the Korean Nuclear Society Conference. (2005) 313-314. Corpus ID: 220264966

[16] M.S. Kim, B.S. Kim, J.M. Yoo, K.K. Yoo, J.C. Lee, W.B. Kim, Reductive precipitation of platinum and palladium with hydrazine in hydrochloric acid solution, Journal of the Korean Institute of Metals and Materials, 46 (4) (2008) 233-240

[17] S.J. Song, V.N.H. Nguyen, M.S. Lee, Separation of Pd(II) and Zn(II) by solvent extraction using commercial extractants from the hydrochloric acid leaching solution of cemented Pd from spent electroplating solutions, Korean Journal of Metals and Materials, 60 (2) (2022) 1-10.

[18] A.I. Vogel, Textbook of Quantitative Chemical analysis, 5th, Longman scientific & Technical, New York,1989, p. 295-296

[19] Y. Cao, S. Harjanto, A. Shibayama, I. Naitoh, T. Nanami, K. Kasahara, Y. Okumura, T. Fujita, Kinetic study on the leaching of Pt, Pd and Rh from automotive catalyst residue by using chloride solutions, Materials Transactions, 47 (8) (2006) 2015–2024. https://doi.org/10.2320/matertrans.47.2015

[20] M.H.H. Mahmoud, Leaching platinum-group metals in a sulfuric acid/chloride solution, JOM, 55 (2003) 37–40. https://doi.org/10.1007/s11837-003-0086-y

[21] M. Hasani, A. Khodadadi, S.M.J. Koleini, A.H. Saeedi, A.M. Meléndez, Simultaneous leaching of Pt, Pd and Rh from automotive catalytic converters in chloride-containing solutions, Journal of Physics: Conference Series 786 (2017) 012042. https://doi.org/10.1088/1742-6596/786/1/012042

[22] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, John Wiley & Sons, New York, 1999, p.992–1014

[23] J.R. Burgess, H. Prince, Zinc: Inorganic & Coordination ChemistryBased in part on the article Zinc: Inorganic & Coordination Chemistry by Reg H. Prince which appeared in the Encyclopedia of Inorganic Chemistry, First Edition. Encycl Inorg Chem, 2006

[24] W.M. Haynes, Handbook of Chemistry and Physics. CRC Press: Boca Raton, FL, USA.96th, Routledge, 2014, p.4-48

[25] S. Harjanto, Y. Cao, A.I. Shibayama, I. Naitoh, T. Nanami, K. Kasahara, Y. Okumura, K. Liu, T. Fujita, Leaching of Pt, Pd and Rh from automotive catalyst residue in various chloride based solutions, Materials Transactions 47(1) (2006) 129 -135. https://doi.org/10.2320/matertrans.47.129

[26] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, London, 1966, p.359 – 591.

[27] J. Gouyon, F. d’Orlyé, J. Zimmerman, S. Griveau, F. Bedioui, A. Varenne, Speciation and quantitation of precious metals in model acidic leach liquors, theoretical and practical aspects of recycling, Analytical and Bioanalytical Chemistry, 412 (2020) 4595-4608. https://doi.org/10.1007/s00216-020-02707-4

SELEKTIVNO TALOŽENJE AMONIJUM HEKSAHLOROPALADATA IZ LUŽNIH RASTVORA CEMENTIRANIH PALADIJUMOM SA CINKOM

V.N.H. Nguyen, S.J. Song, M.S. Lee *

Odsek za naprednu nauku o materijalima i inženjerstvo, Institut za retke metale, Nacionalni univerzitet Mokpo, Republika Koreja

Apstrakt

Koncentracija paladijuma (Pd) prisutnog u istrošenim rastvorima za galvanizaciju vrši se cementacijom uz pomoć metalnog praha cinka (Zn). Zato je potrebno da se Pd dobije iz cementiranog Pd. U ovom radu istraživano je dobijanje čistih Pd(IV) jedinjenja iz rastvora za luženje cementiranog Pd korišćenjem selektivnih metoda taloženja. Nađeno je da je postojanje Pd(IV) u vodenim rastvorima od izuzetnog značaja za taloženje uz pomoć NH_4Cl*. Testirani su eksperimenti taloženja Pd(IV) iz sintetičkog rastvora carske vode sa sadržajem Pd(IV) i Zn(II). Nakon toga su primenjeni optimalni uslovi taloženja da bi se dobili Pd(IV) talozi iz pravih* H_2SO_4 *i HCl rastvora za luženje koji sadrže NaClO kao oksidans. Selektivno taloženje je rezulturalo dobijanjem izuzetno čistog* $(NH_4)_2PdCl_6$ *iiz pravih rastvora za luženje pod uslovima molarnog odnosa Pd(IV) prema* NH_4Cl *od 1:30 pri temperaturi od* 60^oC *i u roku od 30 min. Procenat taloženja Pd(IV) iz* H_2SO_4 *i HCl rastvora bio je preko 99.9 and 98.2%, pojedinačno. Za dobijanje čistih Pd(IV) jedinjenja iz istrošenih rastvora za galvanizaciju predložen je jednostavan hidrometalurški proces koji se sastoji od cementacije, luženja i taloženja.*

Ključne reči: *Taloženje; Cementirani Pd; Amonijum heksahloropaladat; Istrošeni rastvor za galvanizaciju; Dobijanje*