

Received October 26, 2021; reviewed; accepted December 01, 2021

Recovery of pure palladium compound from the spent electroplating solutions by hydrometallurgical method

Viet Nhan Hoa Nguyen, Si Jeong Song, Man Seung Lee

Department of Advanced Materials Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 534-729, Republic of Korea

Corresponding author: mslee@mokpo.ac.kr (Man Seung Lee)

Abstract: Electroplating of palladium (Pd) is practiced in the manufacture of electronic materials. The increasing demand for Pd metal necessitates the recovery of Pd(II) from the spent electroplating solutions. In this work, the recovery of Pd compound was studied from the cemented Pd by zinc (Zn) metal from spent electroplating solutions. Initially, the selective extraction ability of ionic liquids synthesized from commercial extractants for Pd(II) over Zn(II) from the synthetic HCl solution was investigated. Pd(II) was selectively extracted over Zn(II) from 9 M HCl solution by ALi-CY301 (*N*-methyl-*N,N,N*-trioctylammonium bis(2,4,4-trimethylpentyl) dithiophosphinic) and by ALi-I (*N*-methyl-*N,N,N*-trioctylammonium iodide) from weak HCl solution (pH 1). Since 9 M HCl was needed to completely dissolve Pd from the cemented Pd, ALi-CY301 was employed for the separation of Pd(II) and Zn(II) from the real HCl leaching solution of the cemented Pd. Two-stages counter-current extraction of the real HCl solution with ALi-CY301 resulted in selective extraction of Pd(II). Pd(II) was effectively stripped from the loaded ALi-CY301 by a mixture of HCl and NaClO. After oxidizing Pd(II) in the stripping solution to Pd(IV) by adding NaClO, Pd(IV) compound was synthesized by adding NH₄Cl as a precipitant. By comparing leaching and extraction efficiency between hydrochloric and sulfuric acid solutions, a hydrometallurgical process consisted of HCl leaching, extraction with ALi-CY301 and precipitation with NH₄Cl was recommended for the recovery of pure (NH₄)₂PdCl₆ from the cemented Pd.

Keywords: leaching, solvent extraction, palladium, separation, precipitation

1. Introduction

Palladium electrodeposition is one of the crucial steps for application of Pd in various electronic devices and advanced materials (Antler, 1982). Owing to the increase in demand for Pd, the recovery of Pd from the secondary sources like spent electroplating solutions is important. For this purpose, Pd in the spent electroplating solutions is first cemented by Zn metal powders with fine size. Therefore, it is necessary to recover pure Pd metal or compounds from the cemented Pd. In practice, leaching of the cemented Pd and then the separation of Pd(II) from the leaching solution is a good option. The surface of the cemented Pd is covered by Pd metal, while Zn metals exist in the interior of the cemented Pd. Pd metal can be dissolved by leaching with HCl or H₂SO₄ solution in the presence of oxidizing agent. Therefore, leaching of the cemented Pd in the presence of oxidizing agent results in a solution containing Pd(II) and Zn(II) (Song, et al., 2021). Hence, to recover Pd(II) with high purity, it is necessary to separate Pd(II) and Zn(II). Several methods such as solvent extraction (Reddy et al., 2010; Gupta and Singh, 2013; Nguyen, et al., 2016; Truong and Lee, 2018), ion exchange (Rovira et al., 1998), and precipitation (Schreier and Edtmaier, 2003) are employed to separate Pd(II) from diverse leachates. Among these methods, solvent extraction has some advantages such as selectivity and high purity of the targeted metal ions in real operation (Cieszynska and Wisniewski, 2011; Pospiech and Chagnes, 2014; Nguyen, et al., 2016; Nguyen, et al., 2020).

Several commercial extractants and ionic liquids (ILs) which have a selectivity for Pd(II) have been reported such as oxime, amines, and acidic extractants (Rane and Venugopal, 2006; Pan and Zhang, 2009; Reddy et al., 2010; Swain et al., 2010; Cieszynska and Wisniewski, 2011; Katsuta et al., 2011; Paiva et al., 2014; Sasaki et al., 2014; Nguyen, et al., 2016; Truong et al., 2017; Truong and Lee, 2018; Nguyen, et al., 2020). Notably, the application of ILs to recover Pd(II) has some merits in terms of selectivity and efficiency. However, the utilization of synthesized ILs derived from commercial extractants as well as ILs with inorganic ions such as I⁻, Br⁻, SCN⁻ for separation of Pd(II) over other metals is still limited. According to HSAB (Hard soft acid base) principle, Pd(II) is a soft acid, while Zn(II) is a border line acid (Burgess and Prince, 2006; Truong and Lee, 2018). Therefore, it is possible to make use of the difference in the hardness between Pd(II) and Zn(II). Compared to Zn(II), Pd(II) has a stronger tendency to form stable anionic complexes with inorganic anions such as I⁻, Br⁻, SCN⁻, which can be selectively extracted into the organic phase (Robert et al., 1976; Colombo et al., 2008; Nguyen, et al., 2020). This motivated us to employ the synthesized ILs for selective extraction of Pd(II) over Zn(II) from hydrochloric acid solution.

We have done solvent extraction experiments with ILs from the synthetic sulfuric acid leaching solutions of cemented Pd (Nguyen, et al., 2021). According to this work, ALi-LIX63 (*N*-methyl-*N,N,N*-trioctylammonium 5,8-diethyl-7-hydroxydodecane-6-oxime) and ALi-LIX84 (*N*-methyl-*N,N,N*-trioctylammonium 2-hydroxy-5-nonylacetophenone oxime) were able to selectively extract Pd(II) over Zn(II) when sulfuric acid concentration was in the range from 0.5 to 9 M. In leaching of the cemented Pd with sulfuric acid solutions, oxidizing agent is necessary to dissolve Pd metal. According to our work (Song et al., 2021), NaClO is effective in dissolving Pd with sulfuric acid solution, while H₂O₂ cannot dissolve Pd. When we applied ALi-LIX63 and ALi-LIX84 to separate Pd(II) from the real sulfuric acid solutions of cemented Pd, it was difficult to separate the two metal ions owing to co-extraction of some amount of Zn(II). This extraction of Zn(II) can be ascribed to the existence of chloride ion resulted from the reduction of NaClO during leaching of Pd metal. To develop an efficient process for the recovery of pure Pd(II) from cemented Pd, it is necessary to compare the leaching and separation performance between hydrochloric and sulfuric acid solutions.

Therefore, the objective of this work was to find a suitable IL for the separation of Pd(II) and Zn(II) from hydrochloric acid solution of cemented Pd from spent electroplating solutions. To investigate the extraction behavior of metals, two kinds of ILs with organic (ALi-D2 (*N*-methyl-*N,N,N*-trioctylammonium bis(2-ethylhexyl)phosphoric), ALi-PC (*N*-methyl-*N,N,N*-trioctylammonium 2-Ethylhexyl 2-ethylhexyphosphonic), ALi-CY301, ALi-CY272 (*N*-methyl-*N,N,N*-trioctylammonium bis(2,4,4-trimethylpentyl) phosphinic), ALi-LIX 63, ALi-LIX 84) and inorganic anions (ALi-I, ALi-Br (*N*-methyl-*N,N,N*-trioctylammonium bromide), ALi-SCN (*N*-methyl-*N,N,N*-trioctylammonium thicyanate)) were employed in this work. The effect of HCl concentration on the extraction behavior of Pd(II) and Zn(II) by the ILs was investigated in the HCl concentration range from 0.5 to 9 M. From these results, some ILs which showed selectivity for Pd(II) were selected. The optimum extraction and stripping conditions for the suitable ILs were obtained. Moreover, batch simulation experiments for the counter-current extraction were performed on the basis of the McCabe-Thiele diagrams constructed in this work. Pd compound with high purity was recovered from the stripping solution by first oxidizing Pd(II) to Pd(IV) and precipitating the Pd(IV) with NH₄Cl. From the obtained results, a process was proposed to recover pure Pd compound from the real hydrochloric acid leaching solution of cemented Pd.

2. Experimental

2.1. Reagents and chemicals

For the preliminary experiments, synthetic hydrochloric acid leaching solutions containing Pd(II) and Zn(II) were prepared by dissolving PdCl₂ (Alfa Aesar, Ward Hill, MA, USA, 99.9%) and ZnCl₂ (Duksan Co., Kyungki-do, Korea, 99%) in HCl solution. The concentration of Pd(II) and Zn(II) in synthetic leaching solution was adjusted to 100 mg/L and 500 mg/L, respectively. The acidity of the synthetic solution was controlled from 0.5 to 9 M by adding HCl (Daejung Co., Shiheung, Korea, 35%) solution. Sodium hydroxide (Duksan Co., Kyungki-do, Korea, >99%) was added to adjust the pH of the solution. For stripping experiments, HCl, HNO₃ (Daejung Co., Shiheung, Korea, 60%), H₂SO₄ solutions, thiourea ((NH₂)₂CS, Daejung Co., Shiheung, Korea, > 96%), NaClO (Sigma-Aldrich Co., with available chlorine

10–15%, USA), NH_3 (Junsei Co., Tokyo, Japan, 28%) solutions were used and these agents were diluted by distilled water to the desired concentrations. Ammonium chloride (NH_4Cl , Duksan Co., Gyungki-do, Korea, 99%) was used as a precipitant for Pd(IV).

PC 88A (95%), Cyanex 272 (85%) and Cyanex 301 (70%) were products of Cytec Inc., Saddle Brook, NJ, USA. D2EHPA (95%) and LIX 63 (70%) were purchased from Daihachi Chem., Osaka, Japan and IS Chem. Co., Seoul, Korea, respectively. Aliquat 336 (93%) and LIX 84 (99.9%) were provided by BASF Co., Ludwigshafen, Germany. All extractants were employed without further purification. The extractants were diluted in kerosene (Daejung Co., Shiheung, Korea, > 90%) to obtain the desired organic phases. To avoid the formation of a third phase, decanol (Daejung Co., Shiheung, Korea, > 98%) was added into organic solution (10%v/v) as a modifier and all the employed chemicals were of analytical grade.

Ionic liquids (ILs) were prepared according to the literature as follows. ALi-D2, ALi-PC, ALi-CY272 (ALi represents Aliquat 336) were synthesized by the reported method (Fortuny et al., 2012). ALi-SCN was prepared by contacting Aliquat 336 ($\text{R}_4\text{N Cl}$) and an aqueous solution of 1.6 M KSCN in several times for the complete conversion of chloride to thiocyanate (Preston, 1982; Nayl, 2010). ALi-CY301, ALi-LIX 63 and ALi-LIX 84 were synthesized according to the previous work (Nguyen et al., 2021). In these cases, chloride precipitation using AgNO_3 was performed to verify the transfer of the chloride ions from the organic phase to the aqueous phase. ALi-I and ALi-Br were prepared according to the literature (Nguyen et al., 2020) by reacting Aliquat 336 and 3 M KI or KBr solutions three times.

2.2. Experimental procedure and analytical methods

The extraction (except counter-current extraction) and stripping experiments were carried out at ambient temperature ($22 \pm 1^\circ\text{C}$) by mixing equal volume of the aqueous and organic phase (10 mL each) in a screwed cap bottle. After shaking the mixture for 30 min using a Burrell wrist action shaker (model 75, Pittsburgh, PA, USA), the two phases were then disengaged by keeping them in a glass separatory funnel for 30 min. The concentration of Pd(II) and Zn(II) in the aqueous phase before and after extraction was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos, Cleve, Germany). The concentration of metal ions in the organic phase was calculated from the difference between the metal concentration in the aqueous phase before and after extraction by mass balance. Solution pH was measured by using a thermal scientific pH meter (model A211, Orion Star, Thermo Scientific, Waltham, MA, USA).

Based on the mass of the metal ions in the aqueous phase before extraction $[M]_i$ and after extraction $[M]_a$, the extraction percentage (%E) was calculated as: $\% E = (([M]_i - [M]_a) \times 100) / [M]_i$. The stripping percentage (S%) of a metal ion was defined as: $\% S = ([M]_a^* \times 100) / [M]_o$, where $[M]_o$ and $[M]_a^*$ are the mass of a metal ion in the loaded organic phase before stripping and in the aqueous phase after stripping, respectively. The experiments were done twice and the errors related to the extraction and stripping percentages were around $\pm 5\%$.

The precipitation of Pd(IV) was performed as follows: (i) Pd(II) in the stripping solution was oxidized to Pd(IV) by adding NaClO solution; (ii) addition of NH_4Cl as a precipitant to the solution. The reaction mixtures were stirred by a magnetic stirrer in a heating mantle to control the temperature, time, and stirring speed. Precipitates were collected, and then dried in an oven (Wiseven Wids, Daihan Scientific Co., Korea) at 80°C for overnight. 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 distilled water and then the concentration of Pd(IV) was measured by ICP-OES. The precipitation percentage (P%) of Pd(IV) was calculated as: $P\% = (([M]'_i - [M]) / [M]'_i) \times 100$, where $[M]'_i$ and $[M]$ are the mass of metal ion in the corresponding aqueous phases before and after the precipitation, respectively.

3. Results and discussion

3.1. Effect of HCl concentration on the separation of Pd(II) over Zn(II)

The concentration of Pd(II) in spent electroplating solutions depends on electroplating conditions. In order to increase the recovery percentage of Pd from the spent electroplating solutions, excess amount

of zinc metal is employed in the cementation of Pd(II). Therefore, the concentration of Pd(II) and Zn(II) in the leaching solution would depend on the composition of the cemented Pd and leaching conditions (Song et al., 2021; Nguyen et al., 2021). In this study, the concentration of Pd(II) and Zn(II) in synthetic HCl leaching solution was kept at 100 and 500 mg/L, respectively. The excess concentration of Zn(II) compared to Pd(II) was used in these experiments in order to study the effect of Zn(II) on selective separation of Pd(II).

Pd(II) and Zn(II) in HCl solution can exist as anionic species such as PdCl_4^{2-} and ZnCl_4^{2-} due to the interaction between Pd(II) and Zn(II) with chloride ion (Pospiech and Chagnes, 2014; Wei et al., 2016; Song et al., 2021). Pd(II) has a stronger tendency to form stable complexes with inorganic anions such as SCN^- , I^- and Br^- compared to that of Zn(II), which can be employed for the selective separation of the two metal ions (Elding, 1972; Elding, 1978; Elding and Olsson, 1986; Shi and Elding, 1998; Burgess and Prince, 2006; Colombo et al., 2008; Le Roux et al., 2014). Thus, ILs derived from Aliquat 336 and inorganic anions (SCN^- , I^- and Br^-) such as ALi-SCN, ALi-I and ALi-Br were employed for the selective extraction of Pd(II) over Zn(II) in the HCl solution. Besides, ILs such as ALi-D2, ALi-PC, ALi-CY272, ALi-CY301, ALi-LIX63, ALi-LIX84 were also employed to investigate the separation efficiency of two metals under the same experimental conditions.

To investigate effect of HCl concentration on the separation of Pd(II) over Zn(II), the HCl concentration in the solution was varied from 0.5 to 9 M. Concentration of ILs was fixed at 0.1 M and the volume ratio of the two phases was controlled to unity. In the case of ILs with organic anions, Fig. 1 shows that the extraction behavior of Pd(II) and Zn(II) by ALi-CY272, ALi-D2, ALi-PC was similar. The extraction percentage of Pd(II) and Zn(II) decreased from above 65% to below 40% as HCl concentration increased from 0.5 to 9 M. Meanwhile, ALi-CY301 can completely extract Pd(II) in the studied HCl concentration range, whereas the extraction percentage of Zn(II) decreased from 100 to 59.4%. These results were attributed to the strong interaction between Pd(II) and the sulfur atoms in organic anions of CY301 according to HSAB principle. Besides, the decrease in Zn(II) extraction with the increase of HCl concentration may be related to the competitive extraction of HCl by ILs (Tran and Lee, 2020). The extraction reaction of Pd(II) and Zn(II) by ALi-CY 272/ALi-D2/ALi-PC/ALi-CY301 can be expressed as:



where $[\text{R}_4\text{N}]^+[\text{A}]^-$ denotes ALi-CY 272/ALi-D2/ALi-PC/ALi-CY301, Me is Pd(II)/ Zn(II), the subscript (a) and (o) represent the aqueous and organic phase, respectively.

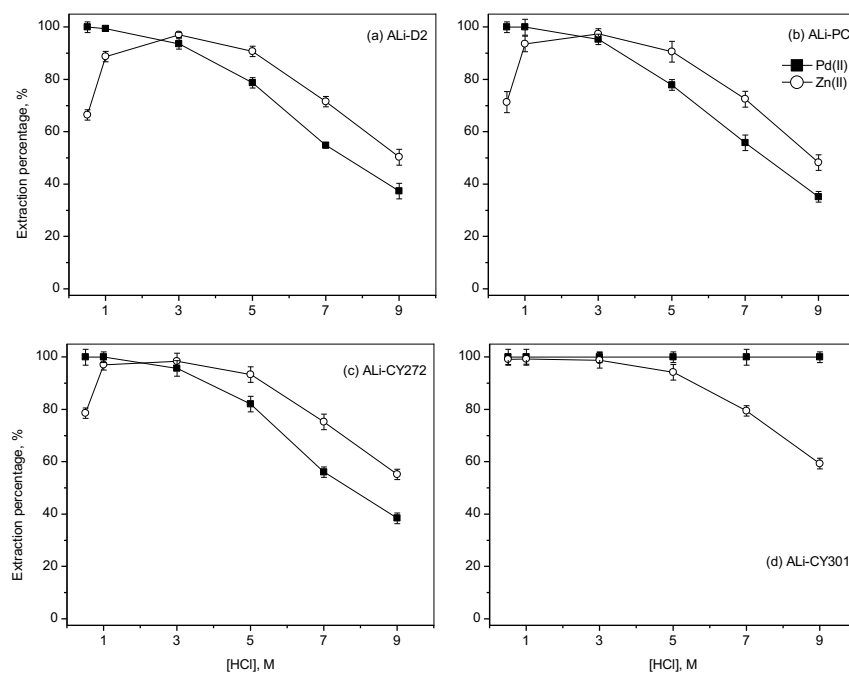
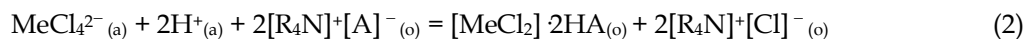


Fig. 1. Effect of HCl concentration on extraction of Pd(II) and Zn(II) by ILs (a) ALi-D2, (b) ALi-PC, (c) ALi-CY272, (d) ALi-CY301 ([IL] = 0.1 M, diluent: kerosene; modifier: decanol 10% v/v. A/ O = 1; [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L)

The influence of HCl concentration on extraction of Pd(II) and Zn(II) by ILs such as ALi-LIX63 and ALi-LIX84 is exhibited in Fig. 2. Pd(II) was completely extracted by ALi-LIX63 and ALi-LIX84 when HCl concentration was less than 5 M and 1 M, respectively. The extraction percentage of Zn(II) by ALi-LIX63 increased from 63.3 to 91.0%, while that by ALi-LIX84 was from 61.9 to 95.1% as HCl concentration increased from 0.5 to 3 M. In both ILs, the increase in the HCl concentration led to a decrease in the extraction of Zn(II) to below 62.0%, indicating that the extractability of metal ions by ALi-LIX63/ALi-LIX84 significantly depends on HCl concentration. The extraction reactions of metals by ALi-LIX63 and ALi-LIX84 can be proposed as:



where $[\text{R}_4\text{N}]^+[\text{A}]^-$ is ALi-LIX63/ ALi-LIX84.

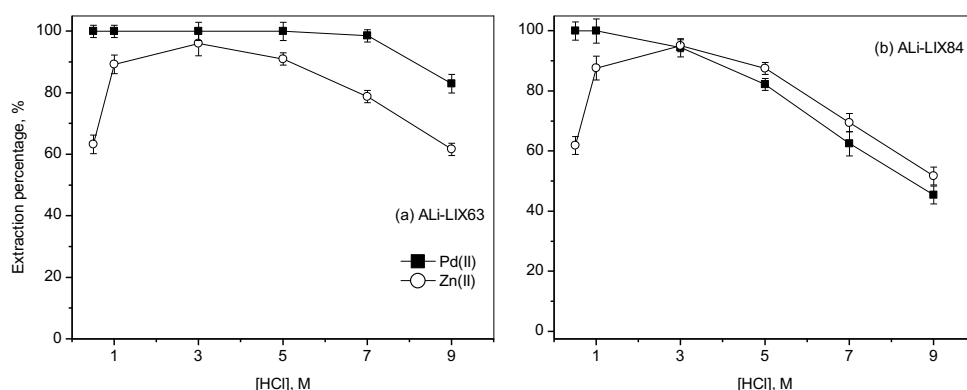
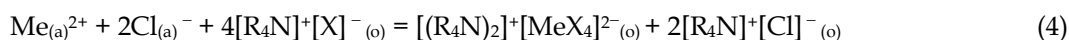


Fig. 2. Effect of HCl concentration on extraction of Pd(II) and Zn(II) by ILs (a) ALi-LIX63, (b) ALi-LIX84 ([IL] = 0.1 M, diluent: kerosene; modifier: decanol 10% v/v. A/ O = 1; [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L)

In the case of ILs with inorganic anions, the effect of HCl concentration from 0.5 to 9 M on the separation of Pd(II) over Zn(II) was also tested under the following conditions: 0.1 M extractant in kerosene; addition of 10% v/v decanol to prevent the formation of a third phase; A/O of 1; the concentration of Pd(II) and Zn(II) was 100 and 500 mg/L, respectively. The effect of HCl concentration on the separation of Pd(II) over Zn(II) by ALi-I, ALi-Br and ALi-SCN is displayed in Fig. 3. The results indicated that Pd(II) was completely extracted by the synthesized ILs such as ALi-SCN, ALi-I regardless of HCl concentration, while Pd(II) extraction by ALi-Br decreased from 100 to 62.4% with the increase of HCl concentration from 0.5 to 9 M. The difference in the extraction behavior of Pd(II) and Zn(II) by ALi-Br and ALi-SCN was negligible. Moreover, the efficient extraction of Zn(II) by ALi-SCN was explained by the formation of $\text{Zn}(\text{SCN})_4^{2-}$ which can be extracted to the organic phase (Hiromitsu and Tatsuya, 1971; Matveichuk et al., 2015). In addition, the decrease in extraction of Zn(II) at a high HCl concentration could be related to the competitive extraction of hydrogen ion by ALi-SCN (Nguyen and Lee, 2020). The extraction of hydrogen ion can cause a decrease in the effective concentration of IL. By contrast, Pd(II) can be selectively extracted over Zn(II) by ALi-I at low HCl concentration (see Fig. 3a). Namely, 99.6% Pd(II) was extracted at 0.5 M HCl, while the extraction percentage of Zn(II) was 33.0%. This can be explained by the difference in complexation degree between Pd(II) and iodide ion compared to Zn(II). Besides, extraction of Zn(II) by quaternary ammonium IL is not favorable at low HCl concentration (Pospiech and Chagnes, 2014). These results indicate that control of solution acidity is important for the selective extraction of Pd(II) by ALi-I. The extraction reaction of Pd(II) by ALi-SCN, ALi-I and ALi-Br is proposed as Eq. (4):



where X is SCN/ I/ Br.

Our results indicate that ALi-CY301 and ALi-I are effective in separating Pd(II) and Zn(II) from HCl solution, while other ILs such as ALi-D2, ALi-PC, ALi-CY272, ALi-LIX63, ALi-LIX84, ALi-SCN, and ALi-Br are not effective in separating the two metal ions. Therefore, further experiments were done by employing ALi-CY301 and ALi-I. Moreover, the acidity of HCl solution has significant effect on the selective extraction of Pd(II) over Zn(II).

In the case of ALi-I, low concentration of HCl was favorable for the selective extraction of Pd(II).

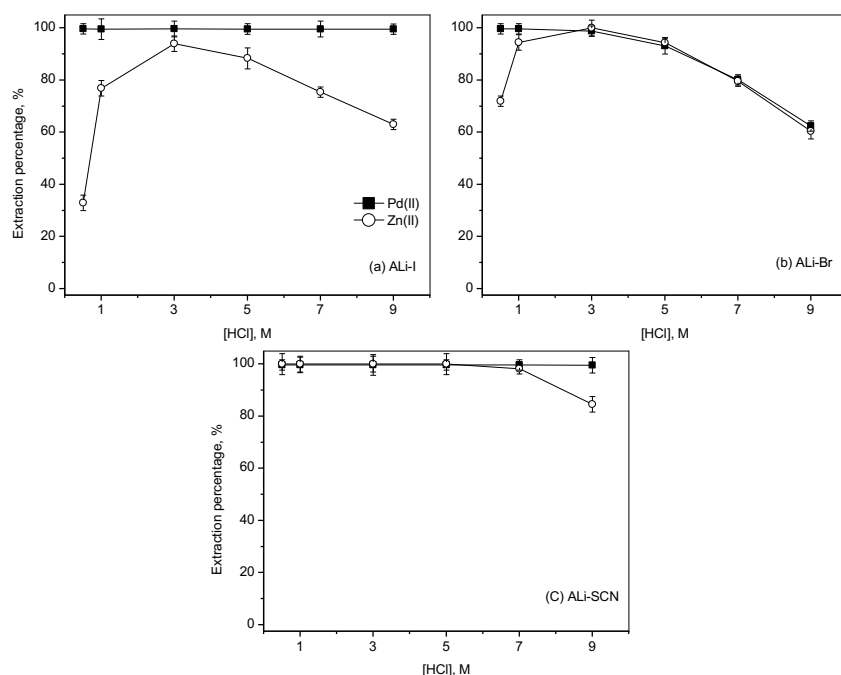


Fig. 3. Effect of HCl concentration on extraction of Pd(II) and Zn(II) by ILs (a) ALi-I, (b) ALi-Br, (c) ALi-SCN ([extractant] = 0.1 M, diluent: kerosene; modifier: decanol 10% v/v. A/ O = 1; [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L)

Therefore, solution pH was varied from 1 to 4 and extraction experiments were done by employing 0.1 M ALi-I at unity phase ratio and the effect of pH on extraction of Pd(II) and Zn(II) by 0.1 M ALi-I is exhibited in Fig. 4. The data show that Pd(II) was completely extracted in this pH range, while Zn(II) extraction was insignificant. In particular, Pd(II) was completely extracted at pH 1, while only 2.5 % of Zn(II) (12.5 mg/L) was extracted. There was little difference between initial pH and equilibrium pH after extraction.

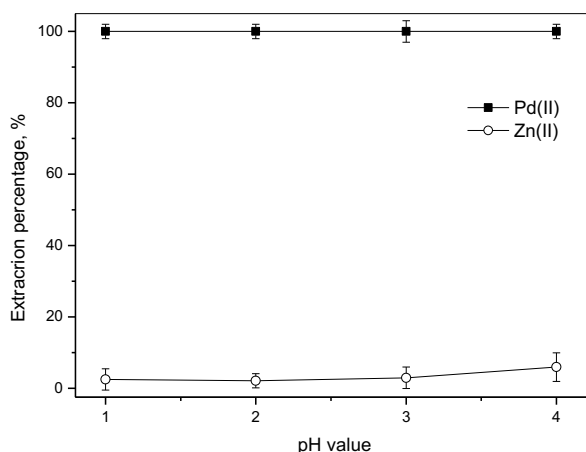


Fig. 4. Effect of pH on extraction of Pd(II) and Zn(II) by 0.1 M ALi-I. (pH = 1-4 M, diluent: kerosene; modifier: decanol 10% v/v. A/ O = 1; [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L)

3.2. The separation of Pd(II) over Zn(II) by using ALi-CY301

In these experiments, the effect of ALi-CY301 concentration on extraction of Pd(II) and Zn(II) was investigated by varying IL concentration from 0.001 to 0.01 M and the results are shown in Fig. 5. The concentration of HCl was fixed at 9 M. The synthetic leaching solution contained 100 mg/L Pd(II) and 500 mg/L Zn(II). The results indicated that selective extraction of Pd(II) was possible with lower concentration of ALi-CY301. Indeed, 81.9 % Pd(II) was extracted by 0.001 M ALi-CY301 while only 4.8 % Zn(II) was extracted (see Fig. 5). The co-extraction of Zn(II) increases with the increase in ALi-CY301

concentration. This can be explained by the strong interaction of ZnCl_4^{2-} with ammonium cation of IL when the concentration of IL was in excess. Therefore, Pd(II) may be completely separated over Zn(II) by employing counter-current extraction. Subsequently, McCabe-Thiele diagram was constructed to estimate the number stages for complete Pd(II) extraction. Fig. 6 is the McCabe-Thiele diagram for the extraction of Pd(II) in 9 M HCl by 0.001 M ALi-CY301, which was constructed by varying the volume ratio of the two phases from 5/1 to 1/5. McCabe-Thiele plot in Fig. 6 indicates that two stages counter-current extraction is necessary for the complete extraction of Pd(II) at an A/O ratio of 2/3. On the basis of the McCabe-Thiele diagram, batch simulation experiments for two stages counter-current extraction were done. The concentration of the metal ions in each stage and the overall extraction percentage are listed in Table 1. As expected, after two stages of counter-current extraction, Pd(II) was completely extracted while no Zn(II) was extracted at all. The loaded organic phase contained 69.2 mg/L Pd(II).

Table 1. Results from batch simulation experiments for two stages counter-current extraction by 0.001 M ALi-CY301 (A/O = 2/3; diluent: kerosene; modifier: decanol 10% v/v; 9 M HCl)

Metal ions	Pd(II)	Zn(II)
Stock solution, mg/L	100.0	500.0
Stage 1, raffinate, mg/L	9.0	501.9
Stage 2, raffinate, mg/L	0.0	500.6
Overall %E	100	0

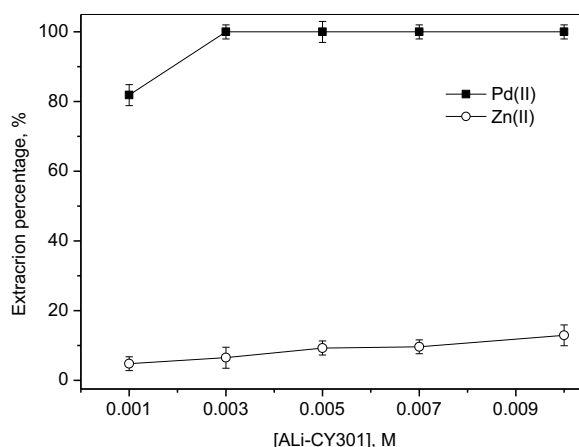


Fig. 5. Effect of ALi-CY301 concentration on extraction of Pd(II) and Zn(II) ([ALi-CY301] = 0.001-0.01 M, diluent: kerosene; modifier: decanol 10% v/v. A/O = 1; 9 M HCl; [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L)

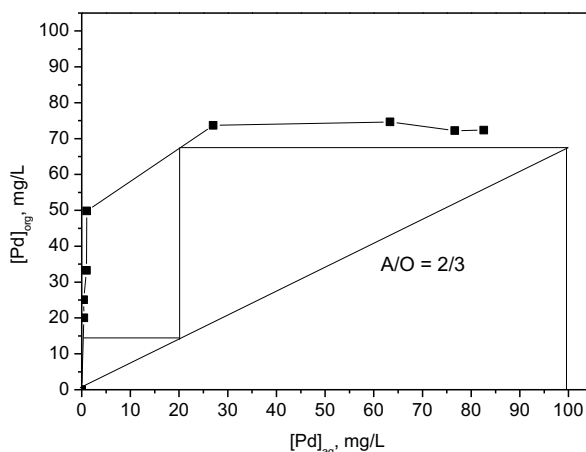


Fig. 6. McCabe-Thiele diagram for extraction of Pd(II) by ALi-CY 301 ([ALi-CY301] = 0.001M, diluent: kerosene; modifier: decanol 10% v/v. A/O = 1/5-5/1, 9 M HCl; [Pd(II)] = 100 mg/L)

It was reported that the stripping of Pd(II) from the loaded ALi-CY 301 was a challenge due to the strong affinity between Pd(II) and sulfur atom of Cyanex 301 (Nayl, 2010). In order to find an appropriate stripping agent for Pd(II) from the loaded ALi-CY301 IL phase, several stripping agents such as HCl, H₂SO₄, NH₃, diluted aqua regia solution, a mixture of HCl and NaClO, and a mixture of HCl and thiourea were tested. **Table 2** displays the stripping percentage of Pd(II) from the loaded ALi-CY301. Among the studied stripping agents, the stripping efficiency of Pd(II) by using the mixture of 5 M HCl and 2% NaClO was the highest (100%, A/O =1). This indicates that the interaction between Pd-chloro complex and ALi-CY301 is so strong that it needs a strong oxidizing agent in acidic solution for a quantitative stripping of Pd(II). Hence, the influence of NaClO and HCl concentration on Pd(II) stripping was investigated by varying their concentration from 0.1 to 2% (v/v) and from 1 to 5 M, respectively and the data are shown in Table 3. The results indicate that Pd(II) was quantitatively stripped with a mixture of 5 M HCl and 0.1% NaClO, and the complete stripping was obtained with the further increase of NaClO concentration from 0.5%. Therefore, concentration of NaClO was kept at 0.5% to find an adequate HCl concentration in the mixture. The results revealed that stripping percentage of Pd(II) increased from 33.7 to 100% as HCl concentration increased in the mixture from 1 to 3 M, and the complete stripping was possible from 3 to 5 M HCl. Consequently, the mixture of 3 M HCl and 0.5% NaClO is the favorable stripping agent for Pd(II) from the loaded ALi-CY301. The stripping reaction of Pd(II) can be proposed as follows:



Table 2. Stripping percentage of Pd(II) from the loaded IL phase of ALi-CY301 using diverse reagents ([ALi-CY301] = 0.001 M, A/O = 1, [Pd(II)] in the loaded phase was 69.2 mg/L)

Stripping agent	Stripping percentage, %
3 M NH ₃	8.8
5 M H ₂ SO ₄	1.6
5 M HCl	4.3
5 M HCl + 2% NaClO	100
5 M HCl + 0.5 M Thiourea	56.4
Aqua regia dilute 1.5 times	76.3

Table 3. Effect of NaClO and HCl concentration on stripping Pd(II) from the loaded organic after two stages counter-current extraction with 0.001 M [ALi-CY301] (A/O = 1; [Pd(II)] in the loaded phase was 69.2 mg/L)

Effect of NaClO concentration	Stripping percentage, %	Effect of HCl concentration	Stripping percentage, %
5 M HCl + 0.1% NaClO	93.4	1 M HCl + 0.5% NaClO	33.7
5 M HCl + 0.5% NaClO	100	2 M HCl + 0.5% NaClO	75.2
5 M HCl + 1.0% NaClO	100	3 M HCl + 0.5% NaClO	100
5 M HCl + 1.5% NaClO	100	4 M HCl + 0.5% NaClO	100
5 M HCl + 2.0% NaClO	100	5 M HCl + 0.5% NaClO	100

3.3. The separation of Pd(II) over Zn(II) by using ALi-I

To investigate the effect of ALi-I concentration on the selective extraction of Pd(II) over Zn(II), the concentration of IL was varied from 0.001 to 0.1 M and the results are exhibited in Fig. 7. The synthetic leaching solution contained 100 mg/L of Pd(II) and 500 mg/L of Zn(II) and solution pH was adjusted to 1. In Fig. 7, the extraction percentage of Pd(II) increased from 86.2 to 100% when the concentration of ALi-I increased from 0.001 to 0.005 M and then constant with the increase of ALi-I concentration. A small amount of Zn(II) was also extracted at this condition (from 1.2 to 2.5%). Therefore, counter-current extraction was performed to depress the co-extraction of Zn(II). Similar to the case of ALi-CY301, batch simulation experiments on the two stages counter-current extraction with an A/O of 2/3 were tried by using 0.001 M ALi-I at pH 1. Table 4 lists the experimental results for two stages counter-current extraction and overall extraction percentage of Pd(II) and Zn(II) by 0.001 M ALi-I. The results revealed

that Pd(II) was completely extracted after two stages counter-current extraction. The concentration of Pd(II) in the loaded IL was 69.2 mg/L Pd(II).

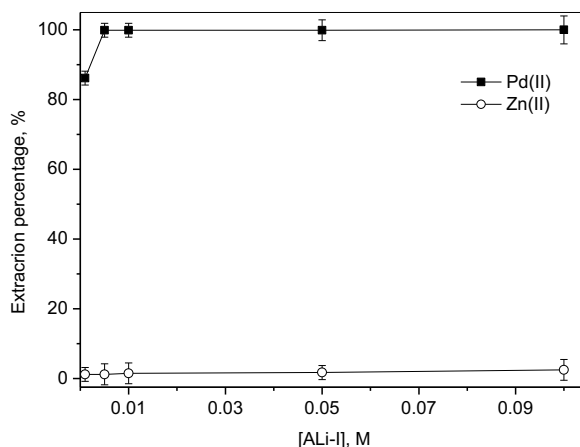
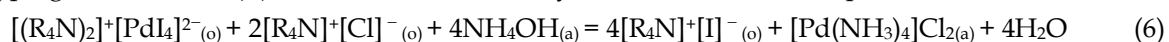


Fig. 7. Effect of ALi-I concentration on extraction of Pd(II) and Zn(II). ([ALi-I] = 0.001-0.1 M, diluent: kerosene; modifier: decanol 10% v/v. A/O = 1, pH = 1; [Pd(II)] = 100 mg/L and [Zn(II)] = 500 mg/L)

Table 4. Batch simulation experimental results for two stages counter-current extraction by 0.001 M ALi-I (A/O = 2/3; diluent: kerosene; modifier: decanol 10% v/v; pH = 1)

Metal ions	Pd(II)	Zn(II)
Stock solution, mg/L	100.0	500.0
Stage 1, raffinate, mg/L	24.2	506.4
Stage 2, raffinate, mg/L	0.0	501.8
Overall %E	100	0

The efficient stripping of Pd(II) from the loaded ALi-I phase was possible by using NH₃ solution (Nguyen et al., 2020). The concentration of NH₃ solution was varied from 0.5 to 3 M to investigate Pd(II) stripping efficiency in this work. **Table 5** illustrates the effect of NH₃ concentration on the stripping of Pd(II) from the loaded organic phase of ALi-I. From the obtained results, the stripping percentage of Pd(II) increased from 81.8 to 95.6% when the concentration of NH₃ increased from 0.5 to 3 M. The stripping reaction of Pd(II) from the loaded ALi-I by NH₃ solution can be represented as



From our obtained results, ALi-CY301 and ALi-I can be considered as promising extractants for the separation of Pd(II) over Zn(II) from hydrochloric acid solutions. Selective extraction of Pd(II) over Zn(II) by these ILs depends on HCl concentrations because there is some difference in the complex formation degree between metal ions and these ligands. Namely, Pd(II) can be selectively extracted by ALi-CY301 at a high concentration of HCl (9 M), while lower concentration of HCl (pH 1) was favorable for ALi-I. The effective stripping of Pd(II) from the loaded ILs was possible by employing either the mixture of HCl and NaClO or NH₃ solution.

Table 5. Effect of NH₃ concentration on the stripping Pd(II) from the loaded organic phase after two stages counter-current extraction with 0.001 M [ALi-I] (A/O = 1; [Pd(II)] in the loaded phase was 69.2 mg/L)

[NH ₃], M	Stripping percentage, %
0.5	81.8
1	85.2
2	86.3
3	95.6

3.4. The separation of Pd(II) over Zn(II) from real HCl leaching solution

Our previous work showed that the complete leaching of Pd and Zn was obtained by employing the mixture of 9 M HCl in presence of 0.5% (v/v) H₂O₂ at 60°C for 60 min (Nguyen et al., 2021). At this condition, the Pd and Zn metal in the cemented Pd were completely dissolved. The concentration of Pd(II) and Zn(II) in the real leaching solution was 1926 mg/L Pd(II) and 74 mg/L, respectively. Since HCl concentration in the real solution was 9 M, ALi-CY301 was more appropriate for the selective extraction of Pd(II). To investigate the effect of ALi-CY301 concentration on separation of Pd(II) over Zn(II) from the real HCl leaching solution, solvent extraction experiments were done by varying ALi-CY301 concentration from 0.001 to 0.1 M at a unity phase ratio. Fig. 8 displays the effect of ALi-CY301 concentration on the extraction of Pd(II) and Zn(II). The results revealed that the extraction efficiency of Pd(II) and Zn(II) is proportion to ALi-CY301 concentration.

As shown in Fig. 8, Pd(II) extraction increased from 8.8 to 100% as ALi-CY301 concentration increased from 0.001 to 0.05 M. The co-extraction of Zn(II) in these experiments was observed when ALi-CY301 concentration was higher than 0.01 M (from zero to 52.9% at 0.1 M ALi-CY301). Therefore, two stages counter-current extraction using 0.01 M ALi-CY301 was employed to depress the co-extraction of Zn(II). Table 6 lists the experimental results for two stages counter-current extraction and overall extraction percentage of the two metal ions by ALi-CY301. The data revealed that Pd(II) can be completely separated from Zn(II) by employing two stages counter-current extraction at an A/O of 2/3. The concentration of Pd(II) in the loaded organic was 1288.3 mg/L, while no Zn(II) was extracted.

The mixture of HCl and NaClO was employed to strip Pd(II) from the loaded 0.01 M ALi-CY301. Our results indicated that 94.8 % Pd(II) (1221.3 mg/L) was stripped with the mixture of 5 M HCl and 0.5% NaClO. Employment of two stages counter-current stripping would lead to complete stripping of Pd(II) from the loaded ALi-CY301. The purity of Pd(II) in the stripping solution was above 99.9%. These

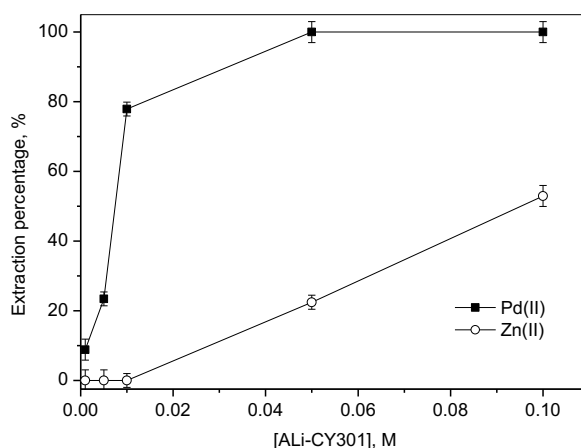


Fig. 8. Effect of ALi-CY301 concentration on extraction of Pd(II) and Zn(II). ([ALi-CY301] = 0.001-0.1 M, diluent: kerosene; modifier: decanol 10% v/v. A/ O = 1, real leaching solution of 9 M HCl; [Pd(II)] = 1926 mg/L and [Zn(II)] = 74 mg/L)

Table 6. Batch simulation experimental results for two stages counter-current extraction by ALi-CY301. ([ALi-CY301] = 0.01M, diluent: kerosene; modifier: decanol 10% v/v. A/ O = 2/3, real leaching solution of 9 M HCl).

Metal ions	Pd(II)	Zn(II)
Stock solution, mg/L	1926.0	74.0
Stage 1, raffinate, mg/L	7.9	73.4
Stage 2, raffinate, mg/L	1.3	74.6
Overall %E	99.9	0.0

results indicate that it is possible to recover pure Pd(II) from the HCl leaching solution of cemented Pd by solvent extraction with ALi-CY301.

In further experiments, recovery of Pd compound was tried by precipitation of Pd(IV) with NH_4Cl . Since Pd(II) in the stripping solution cannot be precipitated by NH_4Cl , a small amount of NaClO (1% v/v) was added to the stripping solution for the oxidation of Pd(II) to Pd(IV) before precipitation. In precipitation experiments, the molar ratio of Pd(IV) to NH_4Cl was fixed at 1:30 and reactions were run at 60°C for 30 min. The results indicated that the precipitation percentage of Pd(VI) was 94.3% with 99.99% purity and the red precipitates were obtained. The morphology and chemical formula of ammonium chloropalladate ($(\text{NH}_4)_2\text{PdCl}_6$) precipitates were verified by the SEM and XRD analysis (see Fig. 9). Hence, the recovery of Pd(IV) compound from the real 9 M HCl leaching solution was achieved with high performance and purity.

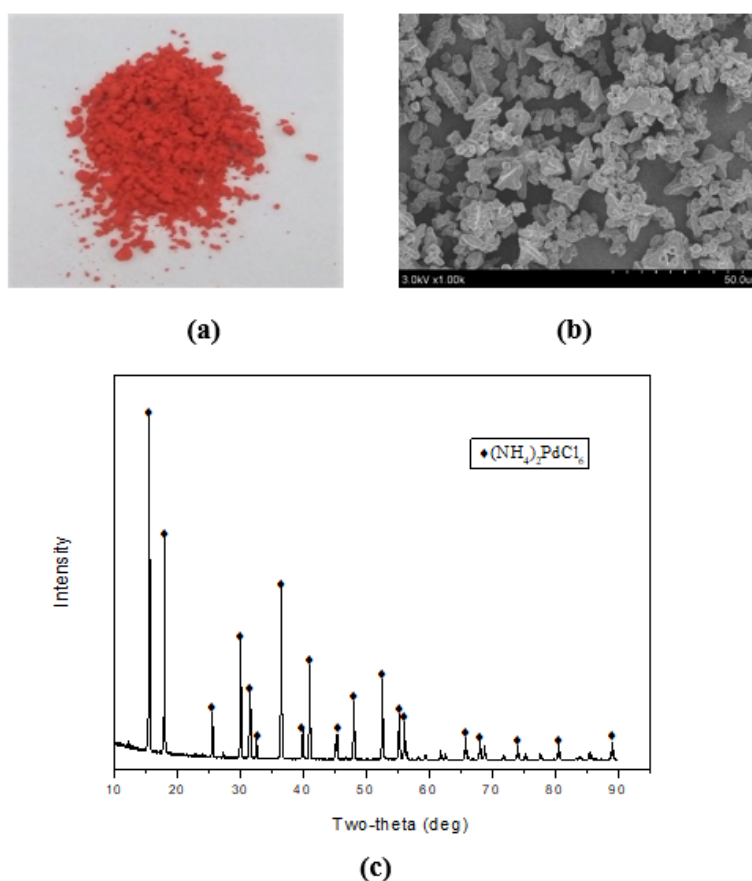


Fig. 9. Powders (a), SEM images (b), and XRD pattern(c) of $(\text{NH}_4)_2\text{PdCl}_6$ precipitates

Based on the obtained results from this study, optimum conditions for the leaching and separation by employing HCl solution are summarized in **Table 7**. In the case of leaching, complete dissolution of Pd can be accomplished by using 9 M HCl solution containing H_2O_2 at 60°C . The complete separation of Pd(II) over Zn(II) from the real hydrochloric acid leaching solution was accomplished by extraction with ALi-CY301. The purity of palladium compounds synthesized from the stripping solution was higher than 99.9%.

Table 7. Optimum conditions for the leaching and separation of Pd(II) from the HCl leaching solution of the cemented Pd

Media of real leachate	Leaching	Separation
9 M HCl with 0.5% H_2O_2	Complete dissolution of Pd at 60°C in 60 min and 2 g/L of pulp density.	Selective extraction of Pd(II) over Zn(II) from the real solution was possible by using ALi-CY301. The mixture of 5 M HCl and 0.5% NaClO was effective for the stripping of Pd(II) from the loaded ALi-CY301.

4. Conclusions

Cemented Pd powders are produced from the treatment of spent electroplating solutions with zinc metal. In order to develop a process for the recovery of pure Pd compound from the cemented Pd, solvent extraction experiments by synthesized ILs were done by employing synthetic HCl leaching solutions. For this purpose, synthesized ILs such as ALi-D2, ALi-PC, ALi-CY301, ALi-CY272, ALi-LIX 63, ALi-LIX 84, ALi-I, ALi-Br, and ALi-SCN were employed to investigate the extraction behavior of Pd(II) and Zn(II) in the HCl concentration range from 0.5 to 9 M. Among these ILs, ALi-CY301 and ALi-I showed selective and effective extraction ability for Pd(II) over Zn(II). The selective extraction of Pd(II) by two stages counter-current extraction of ALi-I was possible at low HCl concentration (pH 1), while that by ALi-CY301 was possible from 9 M HCl. The complete stripping of Pd(II) from the loaded ALi-I and ALi-CY301 was achieved by 3 M NH₃ solution and a mixture of 3 M HCl and 0.5% NaClO solution, respectively. Concentrated HCl solution (9 M) containing H₂O₂ was necessary to completely dissolve Pd in the cemented Pd which resulted from real spent electroplating solutions. Therefore, ALi-CY301 was employed for the selective separation of Pd(II) from the real leaching solution of cemented Pd at 9 M HCl. The experimental results confirmed that (NH₄)₂PdCl₆ with 99.99% purity was recovered from the real leaching solution by extraction with ALi-CY301 followed by stripping with the mixture of HCl and NaClO solution and then by precipitating with NH₄Cl. From the obtained results, a hydrometallurgical process consisting of leaching followed by solvent extraction and precipitation can be applied to recover pure Pd compound from the cemented Pd.

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). We gratefully thank the Gwangju branch of the Korea Basic Science (KBSI) for ICP data.

References

- ANTLER, M., 1982. *The Application of Palladium in Electronic Connectors Continuing Studies result in Growing use.* Platinum Metals Rev. 26, 106-117.
- BURGESS, J., PRINCE, R.H., 2006. *Zinc: Inorganic & Coordination Chemistry Based 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. <https://doi.org/10.1002/0470862106.ia260>.
- CIESZYNSKA, A., WISNIEWSKI, M., 2011. *Selective extraction of palladium(II) from hydrochloric acid solutions with phosphonium extractants.* Sep. Purif. Technol. 80, 385-389.
- COLOMBO, C., OATES, C.J., MONHEMIUS, A.J., PLANT, J.A., 2008. *Complexation of platinum, palladium and rhodium with inorganic ligands in the environment.* Plant Geochemistry: Exploration, Environment, Analysis 8, 91-101.
- ELDING, L.I., 1972. *Palladium(II) halide complexes. I. Stabilities and spectra of palladium(II) chloro and bromo aqua complexes.* Inorganica Chim. Acta 6, 647-651. [https://doi.org/10.1016/s0020-1693\(00\)91874](https://doi.org/10.1016/s0020-1693(00)91874).
- ELDING, L.I., 1978. *Stabilities of platinum(II) chloro and bromo complexes and kinetics for anation of the tetraaquaplatinum(II) ion by halides and thiocyanate.* Inorganica Chim. Acta 28, 255-262.
- ELDING, L.I., Olsson, L.F., 1986. *Stabilities, solubility, and kinetics and mechanism for formation and hydrolysis of some palladium(II) and platinum(II) iodo complexes in aqueous solution.* Inorganica Chim. Acta 117, 9-16.
- FORTUNY, A., COLL, M.T., SASTRE, A.M., 2012. *Use of methyltrioctyl/decylammonium bis 2,4,4-(trimethylpentyl)phosphinate ionic liquid (ALi-CY IL) on the boron extraction in chloride media.* Sep. Purif. Technol. 97, 137-141.
- GUPTA, B., SINGH, I., 2013. *Extraction and separation of platinum, palladium and rhodium using Cyanex 923 and their recovery from real samples.* Hydrometallurgy 135,11-18.
- HIROMITSU, M., TATSUYA, S., 1971. *Stability and Extractability of Zinc (II) Thiocyanate complexes in several solvent extraction systems.* Bull. Chem. Soc. Jpn. 44, 3347-3352.
- KATSUTA, S., YOSHIMOTO, Y., OKAI, M., TAKEDA, Y., BESSHO, K., 2011. *Selective Extraction of Palladium and Platinum from Hydrochloric Acid Solutions by Trioctylammonium-Based Mixed Ionic Liquids.* Ind. Eng. Chem. Res 50, 12735-12740.

- LE ROUX, C.J., GANS, P., KRIEK, R.J., 2014. *Complexation of palladium(II) with thiocyanate – a spectrophotometric investigation*. J. Coord. Chem. 67, 1520–1529.
- MATVEICHUK, Y.V., RAKHMAN'KO, E.M., YASINETSII, V.V., 2015. *Thiocyanate complexes of d metals: Study of aqueous solutions by UV, visible, and IR spectrometry*. Russ. J. Inorg. Chem. 60, 100–104.
- NAYL, A.A., 2010. *Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336*. J. Hazard. Mater. 173, 223–230.
- NGUYEN, T.H., SONU, C.H., LEE, M.S., 2016. *Separation of Pt(IV), Pd(II), Rh(III), and Ir(IV) from concentrated hydrochloric acid solutions by solvent extraction*. Hydrometallurgy 164, 71–77.
- NGUYEN, V.N.H., LEE, M.S., 2020. *Solvent extraction of Hydrochloric Acid Using Commercial Extractants and Synthesized Ionic Liquids*. J Korean Inst Resour Recycl. 29, 79–87.
- NGUYEN, V.N.H., SONG, S.J., LEE, M.S., 2021. *Recovery of pure Pd(II) from spent electroplating solutions by solvent extraction with ionic liquids from sulfuric acid leaching solution of cemented Pd*. Metals. <https://doi.org/10.3390/met11081320>.
- NGUYEN, V.T., RIAÑO, S., BINNEMANS, K., 2020. *Separation of precious metals by split-anion extraction using water-saturated ionic liquids*. Green Chem. <https://doi.org/10.1039/d0gc02356f>.
- PAN, L., ZHANG, Z., 2009. *Solvent extraction and separation of palladium(II) and platinum(IV) from hydrochloric acid medium with dibutyl sulfoxide*. Miner. Eng. 22, 1271–1276. <https://doi.org/10.1016/j.mineng.2009.07.006>.
- PAIVA, A.P., CARVALHO, G.I., COSTA, M.C., ROSA DA ROSTA, A.M., NOGUEIRA, C., 2014. *Recovery of platinum and palladium from chloride solutions by a thiodiglycolamide derivative*. Solvent Extr. Ion Exc. 32, 78–94.
- POSPIECH, B., CHAGNES, A., 2014. *Highly Selective Solvent Extraction of Zn(II) and Cu(II) from Acidic Aqueous Chloride Solutions with Mixture of Cyanex 272 and Aliquat 336*. Sep Sci Technol. 50, 1302–1309.
- PRESTON, J.S., 1982. *Solvent Extraction of Cobalt(II) and Nickel(II) by a Quaternary Ammonium Thiocyanate*. Sep. Sci. Technol. 17, 1697–1718.
- RANE, M.V., VENUGOPAL, V., 2006. *Study on the extraction of palladium(II) and platinum(IV) using LIX 84I*. Hydrometallurgy 84, 54–59.
- REDDY, B.R., RAJU, B., LEE, J.Y., PARK, H.K., 2010. *Process for the separation and recovery of palladium and platinum from spent automobile catalyst leach liquor using LIX 84I and Alamine 336*. J. Hazard. Mater. 180, 253–258.
- ROBERT, M., SMITH, A., MARTELL, E., 1976. *Critical Stability Constants. Vol. 4: Inorganic complexes*. Plenum Press, London, pp 1–129.
- ROVIRA, M., CORTINA, J.L., ARNALDOS, J., SASTRE, A.M., 1998. *Recovery and separation of platinum group metals using impregnated resins containing Alamine 336*. Solvent Extr. Ion Exc. 16, 1279–1302.
- SASAKI, K., TAKAO, K., SUZUKI, T., MORI, T., ARAI, T., IKEDA, Y., 2014. *Extraction of Pd(II), Rh(III) and Ru(III) from HNO₃ Aqueous Solution to Betainium Bis-(trifluoromethanesulfonyl)imide Ionic Liquid*. Dalton Trans. 43, 5648–5651.
- SCHREIER, G., EDTMAIER, C., 2003. *Separation of Ir, Pd and Rh from secondary Pt scrap by precipitation and calcination*. Hydrometallurgy 68, 69–75.
- SHI, T., ELDING, L.I., 1998. *Equilibria Kinetics and Mechanism for Complex Formation Between Hydrogen Sulfate/Sulfate and Palladium(II). Hydrolysis of Tetraaquapalladium(II)*. Acta chem. Scand. 52, 897–902.
- SONG, S.J., NGUYEN, V.N.H., LEE, M.S., 2021. *Leaching of the mixture of palladium and zinc metal by hydrochloric and sulfuric acid solutions*. Korean J. Met. Mater.
- SWAIN, B., JEONG, J.K., KIM, S.K., LEE, J.C. 2010. *Separation of platinum and palladium from chloride by solvent extraction using Alamine 300*. Hydrometallurgy 104, 1–7.
- TRAN, T.T., LEE, M.S., 2020. *Interactions Between Ionic Liquid (ALiCY) and TBP and their Use in Hydrometallurgy for Extracting Co(II) and Ni(II)*. Korean J. Met. Mater. 58, 423–432.
- TRUONG, H.T., LEE, M.S., SON, S.H., 2017. *Extraction of Palladium(II) from Hydrochloric Acid Solutions by Solvent Extraction with Mixtures Containing Either Cyanex 301 or LIX 63*. Metals.
- TRUONG, H.T., LEE, M.S., 2018. *Separation of Pd(II) and Pt(IV) from hydrochloric acid solutions by solvent extraction with Cyanex 301 and LIX 63*. Miner. Eng. 115, 13–20.
- WEI, W., CHO, C.W., KIM, S., SONG, M.H., BEDIKAKO, J.K., YUN, Y.S., 2016. *Selective recovery of Au(III), Pt(IV), and Pd(II) from aqueous solutions by liquid–liquid extraction using ionic liquid Aliquat-336*. J. Mol. Liq. 216, 18–24.