

# Effect of Ethylene Glycol on the Dissolution of Palladium with HCl Solution Containing Oxidizing Agents and Selective Precipitation of Pd(IV) Compound

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**Abstract:** There is growing interest in the recovery of pure palladium (Pd) compound from cemented Pd from spent electroplating solutions due to increasing demand for Pd, and there is considerable motivation to develop an efficient recovery process. In conventional methods of leaching Pd metal, HCl solutions containing oxidizing agents are employed. In this work, ethylene glycol (EG) replaced water as a diluent in the HCl solution containing oxidizing agents such as  $H_2O_2$ , NaClO and  $NaClO_3$ . Leaching of the Pd metal and the subsequent precipitation of the Pd(IV) compound was investigated. Among the three kinds of oxidizing agent,  $NaClO_3$  showed the best Pd metal leaching efficiency from a metallic mixture of Pd and Zn from HCl in EG solution. The role of EG in enhancing the leaching and precipitation is discussed in light of its interaction with other components in the solutions. To precipitate the Pd(IV) compound with  $NH_4Cl$ , it is important that the dissolved Pd ion exists as Pd(IV). Therefore,  $NaClO_3$  was again added to the leaching solution to verify the oxidation of Pd(II) to Pd(IV). Extra pure ammonium hexachloropalladate ( $(NH_4)_2PdCl_6$ ) was recovered by precipitation from the leaching solution of the cemented Pd under the optimum conditions. Compared to conventional HCl systems, the present process shows some advantages, by reducing both chemical dosage and energy consumption. The results confirm a process can be developed for the recovery of the Pd(IV) compound from spent electroplating solutions containing a small amount of Pd(II).

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**Keywords:** ethylene glycol; leaching; precipitation; palladium; ammonium hexachloropalladate

## 1. INTRODUCTION

Demand for palladium, one of the precious metals group, is rapidly increasing for the manufacture of catalysts and advanced materials [1-4]. This has inspired many researchers to recover palladium from secondary resources for sustainable production. Lots of work has been conducted on the recovery of palladium from spent catalysts [5-10]. However, the amount of palladium in spent electroplating solution is low and thus few works have been reported on the treatment of spent electroplating solutions [11,12]. To recover Pd(II) from spent electroplating solutions, it is first necessary

to concentrate the Pd(II) by cementation with zinc (Zn) powder [13,14]. Leaching of the cemented Pd metal is then required to recover the pure Pd metal. Further separation steps such as solvent extraction, using either commercial or ionic liquid extractants, ion exchange, or precipitation can be employed to obtain pure Pd(II) solutions or palladium compounds [8,9,11,12,15-18]. Our previous work reported on the use of non-aqueous leaching for the dissolution of Pd metal, providing an alternative approach to enhance Pd dissolution efficiency [19]. It was determined that the presence of TBP (tributyl phosphate)/MIBK (methyl isobutyl ketone) /EG as extractants or diluent in the leaching systems could significantly affect performance of a certain hydrometallurgical process, due to their interaction with other components [19,20].

Ethylene glycol (EG), which can be generated from

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various chemical systems (catalytic and non-catalytic) and biomass-base resources like cellulose is often considered to be a green solvent because of its non-volatility, low flammability, and low toxicity [21,22]. For this reason EG is used as a chemical intermediate in the synthesis of organic chemicals and as an organic solvent in solvo-hydrometallurgy [23,24]. EG has been used as a hydrogen bond donor in eutectic mixtures for effective non-aqueous leaching of flue dust containing Fe, Zn, Pb, Cu, In, and Sn [25]. When EG was used in place of water as a polar solvent in the leaching of metals such as Cu, Co, and Ni, leaching efficiency was enhanced because it stabilized the metal complexes in the leachate [26]. Since the presence of EG reduces the activity of water, the extraction of metal ions to the organic phase is increased [27]. These results suggest it would be worthwhile to investigate the effect of adding EG to a leaching system of HCl containing oxidizing agents for the recovery of palladium from cemented Pd.

The present work investigated the influence of EG on a Pd leaching process consisting of the selective precipitation of the Pd(IV) compound. First, the leaching behavior of Pd and Zn in the metallic mixture by the system of HCl-oxidizing agent-EG was studied, and then selective precipitation of Pd(IV) was analyzed. Subsequently, the optimum conditions were applied to recover the Pd(IV) compound as ammonium hexapalladate precipitate from the leaching solution of cemented Pd.

For this purpose, EG was used in place of water as a polar diluent which contained hydrochloric acid as the leaching agent, and H<sub>2</sub>O<sub>2</sub>, NaClO and NaClO<sub>3</sub> were added as oxidizing agents. The effects of leaching conditions such as temperature, reaction time, acid concentration and the nature of the oxidizing agent were investigated. Among the three oxidizing agents, NaClO<sub>3</sub> showed the best leaching efficiency and thus the leachate containing NaClO<sub>3</sub> was selected for recovery of the Pd(IV) compound by precipitation with NH<sub>4</sub>Cl. Our obtained data indicated that the recovery of pure Pd(IV) compound by leaching cemented Pd, and Pd(IV) precipitation, was favorable in an EG medium.

## 2. EXPERIMENTAL

### 2.1 Reagents and chemicals

Metal powders of Pd (size: 60 mesh, Alfa Aesar, Ward Hill, USA, 99.9%) and Zn (size: 100~200 mesh, Daejung Chemical. Co., Shiheung, Korea, 99.0%) were employed in the leaching experiments. Mixtures of these two metals were prepared by mixing at the same weight ratio. Hydrochloric acid (HCl, Daejung Chemical. Co., Shiheung, Korea, 35%) was diluted in ethylene glycol (EG, Daejung & Metals Co., Korea, >98%) to the obtain desired concentration. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Daejung Chemical. Co., Shiheung, Korea, >30%), NaClO solution (Sigma-Aldrich Co., with available chlorine 10–15%, USA) and NaClO<sub>3</sub> (pure, Daejung Chemical & Metals Co., Shiheung, Korea) were used as oxidizing agents. NH<sub>4</sub>Cl (Duksan Co., Gyungki-do, Korea, 99%) was added as a precipitant. All the employed chemicals were of analytical grade.

### 2.2 Experimental procedure and analytical methods

In the leaching experiments, solutions of HCl in EG with desired volumes and concentration were stirred in a 250 cm<sup>3</sup> three-neck round bottom flask which was placed on a magnetic heating stirrer and a mantle (WiseStir MSH-20D, Daihan Scientific Co., Korea) to control the temperature and stirring speed. After reaching the predetermined temperature, a certain amount of the Pd and Zn mixture and then oxidizing agents were slowly added to the flask to avoid a violent reaction. The cover of the flask was closed to prevent evaporation loss of the reactants. After the leaching was completed, the leaching solution was filtered with filter paper and separated from the residue. Inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro Arcos, Cleve, Germany) was used to measure the concentration of metal ions in the leaching solution. The leaching percentage (%) of component L (L = Pd or Zn) was calculated to be:

$$L (\%) = (m_L/m_o) \times 100\% \quad (1)$$

where  $m_L$  and  $m_o$  are the mass of metal dissolved in the leaching solution and the initial mass of the metal, respectively.

To precipitate the Pd(IV) compound from the synthetic solutions and real leaching solutions, a certain amount of NaClO<sub>3</sub> was added to oxidize Pd(II) to Pd(IV), and then NH<sub>4</sub>Cl was added as precipitant. The reaction mixtures were

**Table 1.** Standard reduction potentials of some reactions at 25°C [29].

Reaction	E°(V)
$\text{Pd}^{2+} + 2\text{e} = \text{Pd}$	0.915
$\text{Zn}^{2+} + 2\text{e} = \text{Zn}$	-0.7626
$\text{PdCl}_4^{2-} + 2\text{e} = \text{Pd} + 4\text{Cl}^-$	0.591
$\text{Cl}_2 + 2\text{e} = 2\text{Cl}^-$	1.36
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} = 2\text{H}_2\text{O}$	1.77
$\text{ClO}_3^- + 6\text{H}^+ + 6\text{e} = \text{Cl}^- + 3\text{H}_2\text{O}$	1.451
$\text{ClO}_3^- + 3\text{H}^+ + 2\text{e} = \text{HClO}_2 + \text{H}_2\text{O}$	1.214
$\text{ClO}_3^- + 6\text{H}^+ + 5\text{e} = 1/2\text{Cl}_2 + 3\text{H}_2\text{O}$	1.47
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e} = \text{Cl}^- + \text{OH}^-$	0.89
$2\text{ClO}^- + 2\text{H}^+ + \text{e} = 0.5\text{Cl}_2 + \text{H}_2\text{O}$	0.83
$\text{ClO}^- + 2\text{H}^+ + 2\text{e} = \text{Cl}^- + \text{H}_2\text{O}$	1.715
$\text{HClO}_2 + 3\text{H}^+ + 4\text{e} = \text{Cl}^- + 2\text{H}_2\text{O}$	1.57

stirred by a magnetic stirrer in a heating mantle. After the reaction, the reaction mixtures were kept for 30 min. Precipitates were collected, washed and then dried in an oven (Wiseven Wids, Daihan Scientific Co., Korea) at 60°C overnight. X-ray diffractometer (XRD, X'Pert-PRO, Empyrean, the Netherlands) and analytical high-resolution scanning electron microscopy (HR-SEM, SU-70, Hitachi, Japan) were used to analyze the characteristics of the precipitates. The purity of the precipitates was verified by dissolving them in 5%  $\text{NH}_3$  solution and then the concentration of the metal ions was measured by ICP-OES. The precipitation percentage (X%) of Pd(IV) was calculated to be:

$$X\% = ((M_i - M)/M_i) \times 100 \quad (2)$$

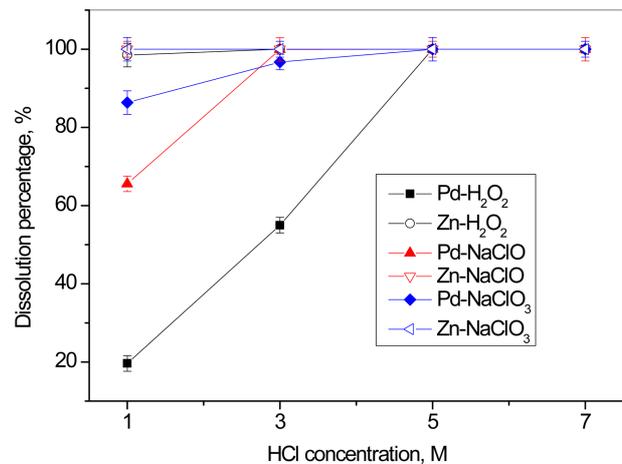
where  $M_i$  and  $M$  are the mass of metal ions in the ethylene glycol phase before and after precipitation, respectively. Experiments were performed two times with errors within  $\pm 5\%$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 Leaching of metallic mixture containing Pd and Zn

##### 3.1.1 Effect of HCl concentration

Since the standard reduction potential of Pd(II) is higher than that of hydrogen ions, the addition of an oxidizing agent is necessary to leach Pd. The standard reduction potentials of



**Fig. 1.** Effect of HCl concentration on dissolution of mixture of Pd and Zn in solvent leaching with presence of oxidizing agent. Conditions: [oxidizing agent] = 0.5 M; [HCl] = 1-7 M; Pulp density = 2 g/L; diluent: ethylene glycol; 60 min; 60°C.

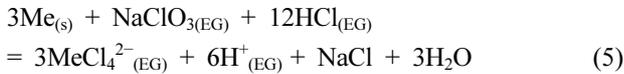
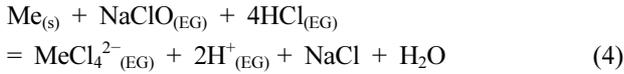
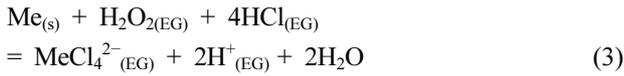
some reactions at 25°C are displayed in Table 1. Among inorganic acidic media, hydrochloric acid is considered to be a better lixiviant than either nitric or sulfuric acid solutions for leaching Pd [28]. In this work, three oxidizing agents,  $\text{H}_2\text{O}_2$ ,  $\text{NaClO}$ ,  $\text{NaClO}_3$ , were added to the HCl in EG solution to compare their leaching performance.

To investigate the effect of HCl on the dissolution of the Pd and Zn mixture, the HCl concentration was varied from 1 to 7 M in EG. The experimental results are shown in Fig. 1. In these experiments, pulp density was kept at 2 g/L, where the weight ratio of Pd to Zn was unity. The reactions were run at 60°C for 60 min. The concentration of oxidizing agent was fixed at 0.5 M. The results indicated that the HCl concentration had a significant influence on the dissolution of Pd and Zn. In the case of  $\text{H}_2\text{O}_2$  and  $\text{NaClO}_3$ , Fig. 1 shows that the dissolution of Pd increased from 19.6 to 100% and from 86.4 to 100% when the concentration of HCl was increased from 1 to 5 M, then became constant with the further increase of HCl concentration. The dissolution of Pd increased from 65.6 to 100% when the HCl concentration was increased from 1 to 3 M in the presence of  $\text{NaClO}$ . Most of the Zn was dissolved in the studied range of HCl concentration. Among the three solvent leaching systems, higher Pd dissolution efficiency was obtained by using either  $\text{NaClO}$  or  $\text{NaClO}_3$  at low concentration in HCl. This result was attributed to the chloride ions released from the reaction

**Table 2.** The stability constants of metal complexes in HCl solution at 25°C [30,31].

Reaction	logK
$Zn^{2+} + Cl^- = ZnCl^+$	0.43
$Zn^{2+} + 2Cl^- = ZnCl_2^0$	0.61
$Zn^{2+} + 3Cl^- = ZnCl_3^-$	0.5
$Zn^{2+} + 4Cl^- = ZnCl_4^{2-}$	0.2
$Pd^{2+} + Cl^- = PdCl^+$	4.47
$Pd^{2+} + 2Cl^- = PdCl_2^0$	7.74
$Pd^{2+} + 3Cl^- = PdCl_3^-$	10.2
$Pd^{2+} + 4Cl^- = PdCl_4^{2-}$	11.5

of NaClO/NaClO<sub>3</sub> [29-31]. Table 2 exhibits the stability constants of metal complexes in HCl solution at 25°C. The dissolution reaction of Pd and Zn by HCl-oxidizing agent-EG can be displayed as

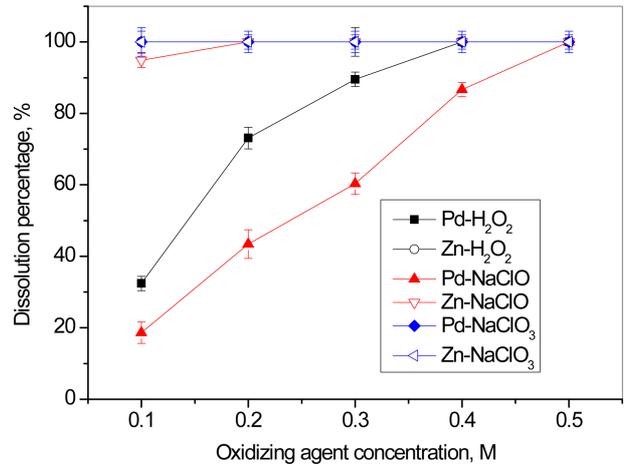


where Me is Pd or Zn

Based on the obtained results, 5 M HCl was used in the presence of H<sub>2</sub>O<sub>2</sub>/NaClO<sub>3</sub> for complete dissolution of the mixture, while the concentration of HCl was controlled to 3 M in the case of NaClO.

### 3.1.2 Effect of oxidizing agent concentration

Adding oxidizing agents to the HCl solution can improve the oxidizing power of the acidic solution for Pd, and their concentration has a great impact on dissolution efficiency [19]. To investigate this influence on the dissolution of Pd and Zn, the concentration of oxidizing agents was varied from 0.1 to 0.5 M. The concentration of HCl was kept at 3 M in the case of NaClO and 5 M for H<sub>2</sub>O<sub>2</sub> and NaClO<sub>3</sub>. These experiments were performed at 60°C within 60 min and pulp density was fixed at 2 g/L. In Fig. 2, the dissolution efficiency of Pd by HCl was in the order of NaClO<sub>3</sub> > H<sub>2</sub>O<sub>2</sub> > NaClO. Pd was completely dissolved in the NaClO<sub>3</sub> concentration range between 0.1 and 0.5 M, while the



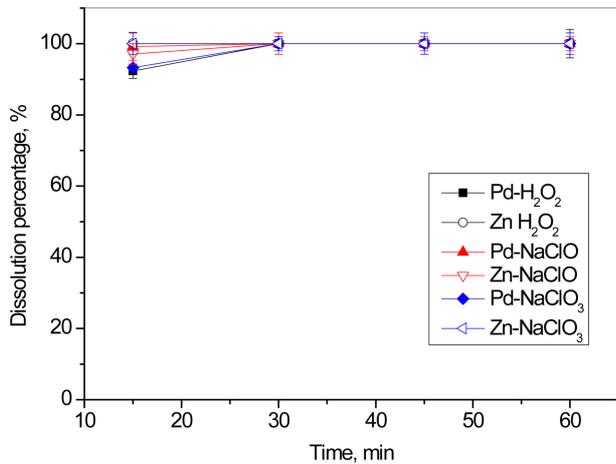
**Fig. 2.** Effect of concentration of oxidizing agent on dissolution of mixture of Pd and Zn. Conditions: [HCl] = 3 M (NaClO) and 5 M (H<sub>2</sub>O<sub>2</sub>/NaClO<sub>3</sub>); [oxidizing agent] = 0.1-0.5 M; Pulp density = 2 g/L; diluent: ethylene glycol; 60 min; 60°C.

dissolution of Pd increased from 32.4 to 100% when the concentration of H<sub>2</sub>O<sub>2</sub> increased from 0.1 to 0.4 M, and then became constant with the further increase of H<sub>2</sub>O<sub>2</sub> concentration. The dissolution of Pd increased from 18.6 to 100% when the NaClO concentration was increased from 0.1 to 0.5 M. Zn was completely dissolved in these experiments.

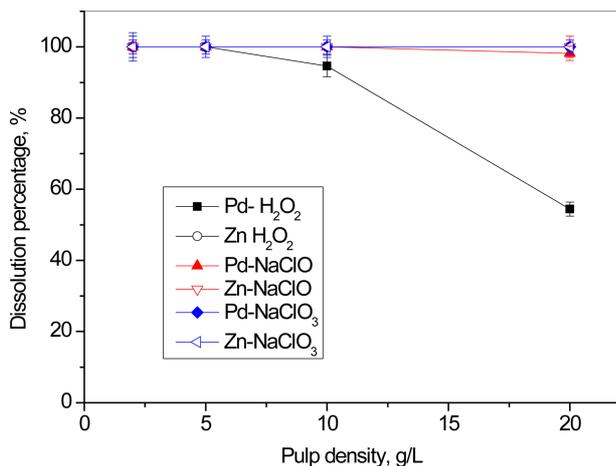
The strongest dissolution power of the leaching system containing NaClO<sub>3</sub> was observed with either a high concentration of HCl (5M) or with the production of intermediate products such as Cl<sub>2</sub> and HClO<sub>2</sub> (E° = 1.36 V and E° = 1.57 V, respectively) which have a strong oxidizing property [29]. With the same concentration of oxidizing agent, the percentage dissolution of Pd was slightly higher with H<sub>2</sub>O<sub>2</sub> than with NaClO. This might be relevant for two reasons: (i) the higher standard reduction potential of H<sub>2</sub>O<sub>2</sub> compared to NaClO (ii) the higher concentration of HCl in the case of H<sub>2</sub>O<sub>2</sub> (5 M).

### 3.1.3 Effect of temperature and time

Leaching experiments were conducted to investigate the effect of temperature and time. In these experiments, the concentration of HCl was fixed at 3 M in the case of NaClO and 5 M in the cases of H<sub>2</sub>O<sub>2</sub> and NaClO<sub>3</sub>, while pulp density was controlled at 2 g/L. Firstly, the effect of temperature on the dissolution of metallic mixture was investigated in the range of 25–80°C. The results revealed that temperature had little effect on dissolution, and the two metals were



**Fig. 3.** Effect of time on the dissolution of Pd and Zn by solvent leaching. Conditions:  $[H_2O_2] = 0.4M$ ;  $[NaClO] = 0.5M$ ;  $[NaClO_3] = 0.1M$  in EG; 5 M HCl in the case of  $H_2O_2$ , NaClO and 3 M HCl in the case of NaClO; Pulp density: 2g/L; 25°C; 500 rpm.



**Fig. 4.** Effect of pulp density on the dissolution of Pd and Zn by solvent leaching. Conditions:  $[H_2O_2] = 0.4M$ ;  $[NaClO] = 0.5M$ ;  $[NaClO_3] = 0.1M$  in EG; 5 M HCl in the case of  $H_2O_2$ , NaClO and 3 M HCl in the case of NaClO; Pulp density: 2-20 g/L; 25°C; 500 rpm.

completely dissolved by the mixture of concentrated HCl and oxidizing agents in EG from 25 to 80°C.

To investigate the effect of reaction time on the dissolution of Pd and Zn, the reaction time was varied from 15 to 60 min. Fig. 3 shows that most of the Pd was dissolved within 15 min. These results indicate that the leaching rate of the metals was fast and both Pd and Zn were completely dissolved within 30 min at 25°C.

### 3.1.4 Effect of pulp density

Experiments were conducted with 5 M HCl in the presence of 0.4 M  $H_2O_2$ , 0.1 M  $NaClO_3$  and 3 M HCl in the case of 0.5 M NaClO at 25°C within 30 min and at a stirring speed of 500 rpm. The effect of pulp density was studied in the range of 2 to 20 g/L (the weight ratio of Pd to Zn was unity) and the results are exhibited in Fig. 4. As shown in Fig. 4, Pd was completely dissolved by the HCl containing  $NaClO_3$  as an oxidizing agent in the pulp density range from 2 to 20g/L. For the HCl- $H_2O_2$ -EG leaching system, Pd was completely dissolved from 2 to 5 g/L of pulp density and decreased to 54.5 % when the pulp density was increased to 20 g/L. In the case of the HCl-NaClO-EG leaching system, the Pd dissolution was complete from 2 to 10 g/L of pulp density and decreased to 98.2 % when the pulp density was increased to 20 g/L. Zn was completely dissolved in these conditions.

The obtained results confirmed that the complete dissolution of metallic mixture of Pd and Zn was possible using the leaching systems of HCl- $H_2O_2$ /NaClO/ $NaClO_3$ -EG. The optimum conditions for dissolution of the mixture containing Pd and Zn are summarized in Table 3. Among the three oxidizing agents,  $NaClO_3$  exhibited the best dissolution efficiency for Pd and Zn with a low concentration of oxidizing agent in EG.

### 3.1.5 Comparison of Pd leaching behavior in the presence and absence of EG

The dissolution efficiency of Pd and Zn metals in two

**Table 3.** The optimum condition of Pd and Zn dissolution by using the leaching system of HCl-oxidizing agent-EG.

Leaching solution	Optimum condition							
	[Agent], M				Pulp density, g/L	Temperature, °C	Time, min	Stirring speed, rpm
	[HCl]	$[H_2O_2]$	[NaClO]	$[NaClO_3]$				
HCl- $H_2O_2$ -EG	5	0.4	-	-	5	25	30	500
HCl-NaClO-EG	3	-	0.5	-	10	25	30	500
HCl- $NaClO_3$ -EG	5	-	-	0.1	20	25	30	500

**Table 4.** Comparison on leaching efficiency between the use of EG and H<sub>2</sub>O (without EG) as diluent (conditions: 25°C, 30 min, 500 rpm).

System	Pulp density, g/L	Leaching percentage, %			
		EG medium		H <sub>2</sub> O medium	
		Pd	Zn	Pd	Zn
5 M HCl-0.4 M H <sub>2</sub> O <sub>2</sub>	5	100	100	15.4	100
3 M HCl-0.5 M NaClO	10	100	100	62.8	87.0
5 M HCl-0.1 M NaClO <sub>3</sub>	20	100	100	52.5	89.2

leaching systems using H<sub>2</sub>O and EG as the diluents, respectively, was compared. Table 4 demonstrates that a higher Pd and Zn dissolution efficiency was obtained by the HCl-NaClO<sub>3</sub>-EG system compared to HCl-NaClO<sub>3</sub>-H<sub>2</sub>O, under the same conditions of 25°C, 30 min, 500 rpm. In particular, complete dissolution of the Pd and Zn was achieved using 3 to 5 M HCl in a leaching system containing EG, while the percentage of Pd and Zn dissolution in the aqueous leaching system was only 63 and 90%, respectively.

In the dissolution of metals, several factors affect the degree of dissolution, such as solvation of the dissolved metal ions, the reduction potential of the metal ions and the stability of the metal complexes in the leaching solution [32,33]. The nature of the solvent affects the dielectric constant of the medium and solvation energy.

Compared to the leaching system with EG, the chloride ions in an aqueous solution are strongly hydrated, thus suppressing the interaction between the metal ions and chloride that would form complexes. Moreover, water contains oxygen donor as a hard base which tends to interact more strongly with a hard acid like Zn(II) than a soft one like Pd(II) according to the hard soft acid base principle. Our results indicate that replacing water with EG in the HCl leaching system in the presence of oxidizing agents enhanced the dissolution of the mixture. This could be related to the stability of [PdCl<sub>4</sub>]<sup>2-</sup> and [ZnCl<sub>4</sub>]<sup>2-</sup> in the EG solution at high HCl concentrations, and the formation of anionic complexes, which can be enhanced in solutions having a lower dielectric constant like EG [34]. Ethylene glycol can solvate and stabilize these metal complexes by hydrogen bonding. Therefore, our results clearly indicate that EG is more

efficient than water as a diluent in the leaching of real cemented Pd.

### 3.2 Precipitation of Pd(IV) from a leaching solution of HCl-NaClO<sub>3</sub>-EG

To recover the Pd(IV) compound from the HCl-NaClO<sub>3</sub>-EG leaching solution, the precipitation of Pd(IV) was investigated by adding NH<sub>4</sub>Cl as a precipitant [35]. In these experiments, the solutions were obtained by leaching the metallic mixture with the same weight ratio. The concentration of Pd ion and Zn(II) in the solution was 1000 mg/L. In order to check the precipitation of Pd compounds from the solution, NH<sub>4</sub>Cl was added to the solution at the molar ratio of Pd ion to NH<sub>4</sub>Cl of 1:30. These experiments were conducted at room temperature for 30 min. The precipitation percentage of Pd compound was only 19.9%. Pd can be dissolved as either Pd(II) or Pd(IV) and the existence of Pd as Pd(IV) is requisite for precipitation with NH<sub>4</sub>Cl to occur [12]. The fact that 19.9% of Pd ion was precipitated indicates that Pd(II) and Pd(IV) coexist in the leaching solution. According to the hard soft acid base principle, the acidity of Pd(IV) is harder than that of Pd(II) because Pd(IV) has a larger charge density. Since NH<sub>3</sub> is a hard base, Pd(IV) has a strong tendency to form coordinate bonds with NH<sub>4</sub><sup>+</sup> rather than Pd(II). This is well demonstrated in the solubility data that showed (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub> was insoluble in water, while (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>4</sub> is soluble [8,29,35].

Therefore, the existence of Pd(IV) as PdCl<sub>6</sub><sup>2-</sup> in the HCl leaching solution is necessary to form a precipitate with NH<sub>4</sub>Cl. In order to oxidize Pd(II) to Pd(IV), 5g/L of NaClO<sub>3</sub> which corresponds to the molar ratio of 1:5 of Pd ion to NaClO<sub>3</sub> was added to the leaching solution, and then NH<sub>4</sub>Cl was added at the molar ratio of Pd ion to NH<sub>4</sub>Cl of 1:30. In these experiments, most of the Pd ions were precipitated as a red colored Pd(IV) compound. From the obtained results, it can be inferred that the addition of enough NaClO<sub>3</sub> is required to dissolve Pd metal as Pd(IV).

To optimize the precipitation performance of Pd(IV), parameters such as the molar ratio of Pd(IV) to either NaClO<sub>3</sub> or NH<sub>4</sub>Cl added (from 1:5 to 1:40), reaction time (from 30 to 120 min), and temperature (25 to 60°C) were investigated. Our data revealed that Pd(IV) was completely

**Table 5.** Comparison on selective Pd(IV) precipitation between aqueous and ethylene glycol media

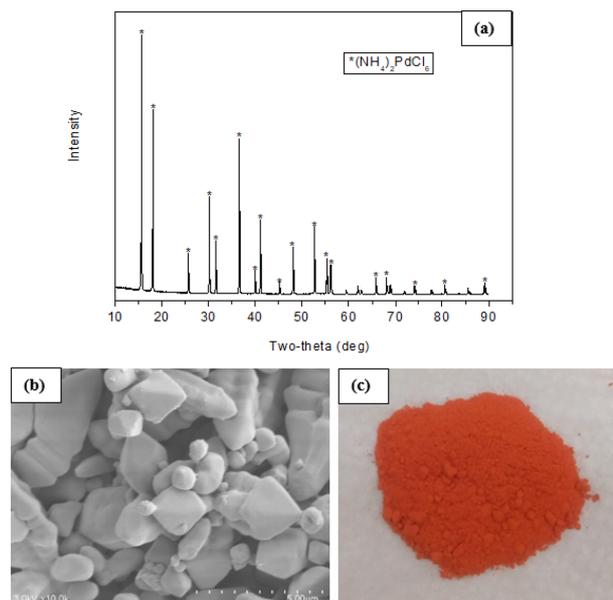
Aqueous media (7 M HCl-1% NaClO-H <sub>2</sub> O leachate) [35]	Ethylene glycol media (5 M HCl-0.1 M NaClO <sub>3</sub> -EG leachate)
- 98.2% Pd(IV) compound was precipitated under conditions: molar ratio, Pd(IV):NH <sub>4</sub> Cl = 1:30; 30 min; 60°C; 500 rpm	- 99.9% Pd(IV) compound was precipitated under conditions: molar ratio, Pd(IV):NaClO <sub>3</sub> added:NH <sub>4</sub> Cl = 1:10:20; 30 min; 25°C; 500 rpm.
- Purity of ammonium chloropalladate ((NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>6</sub> ) precipitates was over 99.99%.	- Addition of NaClO <sub>3</sub> is crucial to oxidize Pd(II) to Pd(IV). - Purity of ammonium chloropalladate ((NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>6</sub> ) precipitates was over 99.99%.

precipitated when the molar ratio of Pd(IV) to NaClO<sub>3</sub> and NH<sub>4</sub>Cl was 1:10:20, at 25°C with 500 rpm of stirring speed within 30 min. Zn(II) was not precipitated under these conditions. This agreed well with the previous work that reported Pd(IV) can be selectively precipitated with NH<sub>4</sub>Cl [35], but the replacement of H<sub>2</sub>O by EG results in some certain benefits. Table 5 displays a comparison of Pd(IV) precipitation efficiency for aqueous and ethylene glycol media. Compared to precipitation in the aqueous solution [35], the precipitation of Pd(IV) in EG was obtained at room temperature. The lower dosage of NH<sub>4</sub>Cl may be related to the decrease in the dissociation of NH<sub>4</sub>Cl in EG because it has a lower dielectric constant ( $\epsilon = 37$ ) than water ( $\epsilon = 80$ ) at room temperature [36].

### 3.3 Recovery of Pd(IV) compound from real leaching solution of cemented Pd

To recover the Pd(IV) compound from the cemented Pd, leaching solutions of cemented Pd were prepared by applying the optimum conditions obtained for the metallic mixture of Pd and Zn, as follows: pulp density of 20 g/L, 5 M HCl and 0.1 M NaClO<sub>3</sub> in ethylene glycol, room temperature, 500 rpm of stirring speed within 30 min. The results showed that complete dissolution of cemented Pd was possible. The concentrations of Pd ions and Zn(II) in the real leaching solution were 19277 mg/L and 723mg/L, respectively.

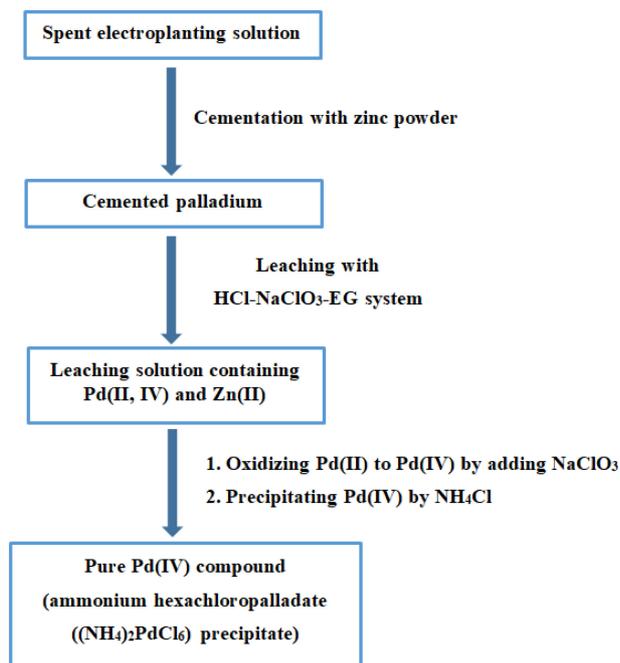
Subsequently, the precipitation of Pd(IV) was carried out by adding a certain amount of NaClO<sub>3</sub> into the leachate in order to oxidize Pd(II) to Pd(IV) and then NH<sub>4</sub>Cl was added to the solution as a precipitant. In these experiments, the molar ratio of Pd(IV) to NaClO<sub>3</sub> and NH<sub>4</sub>Cl was 1:10:20. Reactions were done at room temperature within 30 min and at a stirring speed of 500 rpm. The results show that the precipitation percentage of Pd(IV) was 99.8% under the studied conditions. Zn(II) was not precipitated at all in these experimental conditions. The



**Fig. 5.** XRD pattern (a), SEM images (b), and powders (c) of (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub> precipitates from real leaching solution of cemented Pd.

purity of the Pd(IV) compound was over 99.99%, and XRD analysis confirmed that the chemical formula of precipitate was ammonium hexachloropalladate ((NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub>). The morphology of (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub> was also verified by SEM analysis (see Fig. 5). Our work revealed that pure Pd(IV) compound could be recovered with high performance from cemented Pd using a leaching system of 5 M HCl and 0.1 M NaClO<sub>3</sub> in EG followed by precipitation with NH<sub>4</sub>Cl.

The present process is more efficient than conventional hydrometallurgical processes consisted of leaching followed by solvent extraction [15,16]. Our results clearly show that replacing H<sub>2</sub>O with EG as a polar solvent has a favorable effect on the dissolution of Pd metal from the cemented Pd. Complete dissolution of Pd metal by HCl in EG was possible at room temperature, while at least 60°C was necessary with HCl in water. Moreover, the precipitation of Pd(IV) by



**Fig. 6.** A flowsheet for the recovery of pure Pd(IV) compound from the spent electroplating solution.

$\text{NH}_4\text{Cl}$  from the leaching solution containing EG was enhanced, owing to the reduction in the dielectric constant of the medium [35]. Based on our data, a flowsheet could be proposed for the recovery of pure Pd(IV) compound from the spent electroplating solution (see Fig. 6).

#### 4. CONCLUSIONS

A process was developed for the recovery of pure Pd(IV) compound from cemented Pd from spent electroplating solution. HCl solution diluted with EG was employed as the leaching solution, as an alternative to HCl in water. The effect of oxidizing agents on the dissolution of Pd was investigated using  $\text{H}_2\text{O}_2$ , NaClO, and  $\text{NaClO}_3$ . Among the three oxidizing agents,  $\text{NaClO}_3$  showed the best leaching efficiency for Pd from the metallic mixture of Pd and Zn. Adding  $\text{NH}_4\text{Cl}$  to the solution containing Pd(IV) led to the precipitation of ammonium hexachloropalladate  $(\text{NH}_4)_2\text{PdCl}_6$ . The optimum conditions for leaching were determined to be as follows: 5 M HCl and 0.1 M  $\text{NaClO}_3$  in EG, 20 g/L of pulp density, 25°C within 30 min. By applying these conditions, most of the Pd present in the cemented Pd was recovered as  $(\text{NH}_4)_2\text{PdCl}_6$  with purity higher than 99.9%.

Compared to the solution of HCl in water, that in EG showed some advantages, such as enhancing the dissolution of Pd and the precipitation of Pd(IV) with  $\text{NH}_4\text{Cl}$ . A process can be developed to recover pure Pd(IV) compound from spent electroplating solution by applying our data

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