

# Selective Recovery of Platinum Group Metals from Spent Automotive Catalysts by Leaching and Solvent Extraction

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Platinum group metals (PGMs) play an important role in the automotive industry as key components of exhaust catalysts. Recycling of PGMs from secondary resources, such as waste products, is encouraged to ensure their sustainability. A highly efficient and environmentally benign technique for the separation of PGMs is currently required. In the present study, the recovery of PGMs from a spent automotive catalyst was investigated using the trioctyldecyl phosphonium chloride ( $P_{8,8,8,12}Cl$ ) ionic liquid (IL) as the PGM extraction solvent. First, leaching from the catalyst was investigated. Pt and Pd are selectively extracted into undiluted  $P_{8,8,8,12}Cl$  from the  $5\text{ mol L}^{-1}$  HCl leachate containing various metals together with Pt, Pd, and Rh. Subsequently, Rh is extracted into fresh  $P_{8,8,8,12}Cl$  from the raffinate adjusted to an appropriate HCl concentration. Mutual separation of Pt and Pd is possible by stripping processes. Some common metals co-extracted with PGMs, such as Fe, Cu, and Zn, are removed by each stripping process. Recovery of high purity Pt, Pd, and Rh is achieved by the proposed recycling process. The results demonstrate that separation using phosphonium-based ILs is useful for recycling PGMs.

## Introduction

Platinum group metals (PGMs) are crucially important in various fields, especially in the automotive industry as the key components of exhaust catalysts. Development of exhaust catalysts has significantly increased in recent years because of environmental concerns arising from air pollution. Exhaust catalysts mainly use platinum (Pt), palladium (Pd), and rhodium (Rh) as their main components. The catalytic activity decreases over time and the deactivated catalysts eventually become waste. Disposal of spent catalysts in landfill is restricted because of the presence of harmful leachable substances (Reddy *et al.*, 2010). Accordingly, recycling of spent catalyst waste not only provides economic benefits, but it also contributes to material sustainability (Izatt *et al.*, 2014). Efficient and cost-effective methods to recover PGMs from various spent materials are being pursued. The importance of recovery and recycling approaches for spent industrial and automotive catalysts is also increasing owing to their potential harmful effects.

The main process technologies for recovery of PGMs are categorized as pyrometallurgical methods, selective chlorination processes, and hydrometallurgical methods, such as solvent extraction. Recovery of PGMs by pyrometallurgy requires various processes, which take a long time and consume a large amount of energy. In pyrometallurgical

methods, the ceramic carrier of the catalyst is ground, and then melted with the addition of other metals in the solid or vapor state to produce a PGM alloy and a ceramic waste slag. In recent years, hydrometallurgical methods have attracted attention for PGM recovery. This method has a number of advantages, such as high selectivity, high metal purity, and complete recovery of metals by multi-stage operation (Jha *et al.*, 2013). The solvent extraction process makes it possible to recover valuable metals, such as platinum and palladium, from secondary resources or spent materials, or remove environmentally harmful compounds (Nakashima *et al.*, 2005). When the technique is applied to PGM recycling, the metals contained in the scrap are dissolved in a mineral acid and the leachate is subjected to solvent extraction (Marinho *et al.*, 2010). The leachates from such wastes contain a variety of metal ions along with PGMs. Thus, an efficient process for selective recovery of PGMs with low environmental impact is required.

In recent years, various studies have reported synthesis and application of ionic liquids (ILs). The growing interest in ILs is because of their unique properties, such as their low volatility, low flammability, and low melting point (Regel-rossocka and Wisniewski, 2011). It has recently been found that ILs themselves possess high extraction ability and selectivity for some metal ions, and their application as an extraction solvent (extractant) without dilution has been intensively studied (Yang *et al.*, 2014; Svecova *et al.*, 2016; Kubota *et al.*, 2017). Undiluted phosphonium-based ILs have been applied to the recovery of various metals, such as precious and transition metals (Wellens *et al.*, 2012; Vander Hoogerstraete *et al.*, 2013; Firmansyah *et al.*, 2018).

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In a previous study, we synthesized the phosphonium-based IL trioctyldecyl phosphonium chloride ( $P_{8,8,8,12}Cl$ ) and applied it to metal extraction (Firmansyah *et al.*, 2018). This IL compound was first synthesized in 2011 for other purposes (Adamová *et al.*, 2011). The phosphonium-based IL exhibits excellent performance for extraction and separation of Pt(IV), Pd(II), and Rh(III) in chloride solution.  $P_{8,8,8,12}Cl$  possesses low viscosity and high hydrophobicity, which allows for rapid metal transfer between the aqueous and organic phases. Regeneration and reuse of  $P_{8,8,8,12}Cl$  are also possible with a slight decrease in performance.  $P_{8,8,8,12}Cl$  has also been applied to selective recovery of Pd(II) and Rh(II) from the leachate of an unused automotive catalyst containing Pd(II) and Rh(II) as PGMs and various other metals (Firmansyah *et al.*, 2019).

The aim of this study is to develop an efficient and eco-friendly process for recovering the PGMs from spent automotive catalysts using an IL extraction solvent. The metal components of the waste catalyst depend on the type, model, and year of the vehicle, and the working conditions. In the present study, leaching from a used catalyst was investigated and the metal components were analyzed. Extraction, separation, and recovery of Pt, Pd, and Rh from a real waste automotive catalyst leachate was investigated using undiluted  $P_{8,8,8,12}Cl$  as the extraction solvent. The feasibility of using ILs to recycle valuable metals, such as PGMs, is also discussed.

## 1. Experimental

### 1.1 Reagents

$P_{8,8,8,12}Cl$  was supplied by Nippon Chemical Industrial Co., Ltd. (Tokyo, Japan) (Figure 1).

Pt and Pd standard solutions,  $FeCl_3 \cdot 6H_2O$ ,  $AlCl_3 \cdot 6H_2O$ ,  $ZnCl_2$ ,  $CuCl_2 \cdot 2H_2O$ , and  $MgCl_2 \cdot 6H_2O$  were supplied by Wako Pure Chemical Industries, Ltd.  $LaCl_3 \cdot 7H_2O$ ,  $CeCl_3 \cdot 7H_2O$ , and  $BaCl_2 \cdot 2H_2O$  were supplied by Kishida Chemical Co., Ltd. (Osaka, Japan). Rh standard solution and  $PrCl_3 \cdot 7H_2O$  were supplied by Kanto Chemical Co., Inc., (Tokyo, Japan).  $Na_2SO_3$ ,  $H_2SO_4$ ,  $HNO_3$ ,  $HCl$ ,  $NH_3$ , and  $NaClO_4$  were supplied by Kishida Chemical Co., Ltd. All of the other chemicals were reagent grade, obtained from commercial sources, and used without further purification.

### 1.2 Spent automotive catalysts

A spent catalyst from a gasoline powered vehicle made in Japan was supplied by West-Japan Auto Recycle Co., Ltd. The model year, run distance, and weight of the catalyst are 2000, 85,807 km, and 570 g, respectively. The catalyst carrier

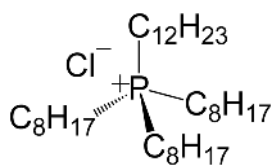


Fig. 1 Molecular structure of  $P_{8,8,8,12}Cl$ .

is ceramic with a honeycomb structure. The spent automotive catalyst block was cut in half lengthwise. The cut surface of the catalyst was analyzed by X-ray fluorescence spectrometry ( $\mu$ XRF, M4 TORANDO plus, Bruker).

### 1.3 Leaching metals from the spent automotive catalyst

Before the leaching process, so that the PGMs could be readily dissolved in acidic solution, the catalyst was mechanically crushed into a fine powder at Seishin Enterprise Co., Ltd., Hibiki Factory (Kitakyushu, Japan) as follows. After crushing the catalyst with a hammer, it was sieved with a 5 mm mesh strainer to produce a coarse powder. The powder was placed in a rotary ball mill with aluminum balls, which was operated for 0.5 to 5.5 h to obtain a fine powder with particle sizes below  $75 \mu m$  (Figure 2) (Tanaka *et al.*, 2012, Gurung *et al.*, 2013).

The leaching test was performed by mixing a specific amount of the powder sample with 50 mL of HCl solution in a round-bottom flask connected with a reflux apparatus for a given time at a controlled temperature on a magnetic stirrer with a dry thermostatic bath (EYELA RCH-20L, Rikakikai Co, Ltd.). The resultant mixture was filtrated and the concentrations of the metal ions in the clear filtrate (i.e., the leachate) were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 8300 Perkin Elmer Co.).

### 1.4 Solvent extraction procedure

The extraction experiment was performed by mixing the aqueous feed solution (leachate) with undiluted  $P_{8,8,8,12}Cl$ . The mixture was agitated with a vortex mixer (Vortex Genie 2, Scientific Industries) for 1 min. It was then shaken in a water bath shaker (NTS-4000, EYELA) at 298 K for a period of time. The mixture was centrifuged at 5800 g for 5 min at 298 K. Metal removal from the loaded IL was performed in a similar manner with each stripping solution. All of the experiments were performed at a 2:1 aqueous phase to IL phase volume ratio, unless otherwise stated. The metal concentrations in the aqueous solution were measured by ICP-AES. The degrees of extraction  $E$  [%] and stripping  $S$  [%] were calculated with the following Eqs. (1) and (2).

$$E = \frac{C_{IL} V_{IL}}{C_{IL} V_{IL} + C_{aq} V_{aq}} \times 100 \quad (1)$$



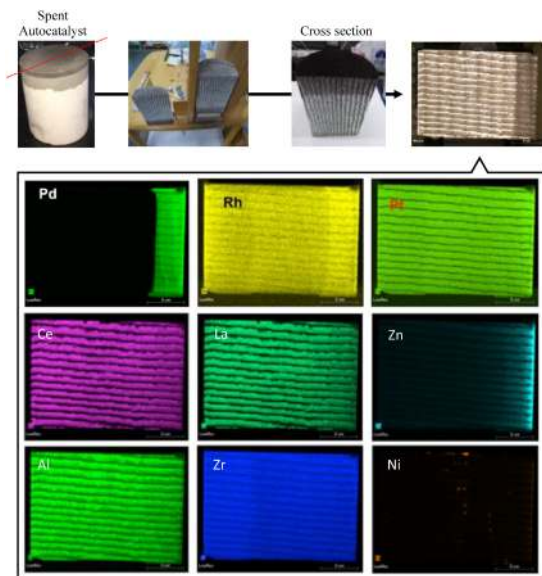
Fig. 2 Spent automotive catalyst pre-leaching treatment

**Table 1** Metal composition of the catalyst determined by  $\mu$ XRF analysis

Metal	Pt	Pd	Rh	Fe	Zn	Cu	Ce	La	Ni	Zr	Mg	Al
[wt%]	0.77	1.52	0.34	0.25	0.09	0.04	6.03	3.37	0.03	15.1	2.61	22.5

**Table 2** Composition of the leachate from the spent automotive catalyst (50 g sample/L 5 mol L<sup>-1</sup> HCl)

Metal	Pt	Pd	Rh	Fe	Zn	Cu	Ce	La	Ni	Zr	Mg	Al
[ppm]	78.7	156.2	26.8	50.2	21.6	8.2	399	523	0.03	0	1016	3792

**Fig. 3** Elemental distribution maps of the cross-section of the catalyst

$$S = \frac{C_{st}V_{st}}{C_{st}V_{st} + C_{IL}V_{IL}} \times 100 \quad (2)$$

Herein,  $V$  [L] and  $C$  [mg L<sup>-1</sup>] are the volume and metal ion concentration, respectively, and the subscripts *aq*, *IL*, and *st* denote the aqueous, *IL*, and stripping phases, respectively.

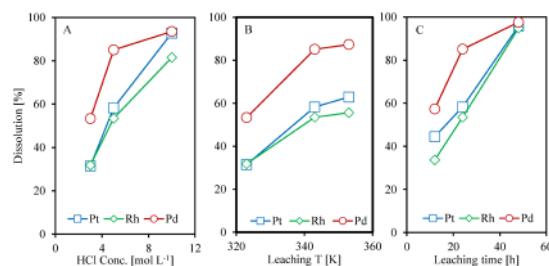
## 2. Results and Discussion

### 2.1 Elemental analysis of the catalyst

The elemental distribution maps of the cross-section of the catalyst determined by  $\mu$ XRF analysis are shown in **Figure 3**. The interior of the catalyst has a honeycomb shape divided into a number of elongated cylinders. The catalyst material is attached to the surface of the wall of the cylinder. Pd, Pt, and Rh are located on the surface, where Pd is only present up to a few centimeters from the end of the catalyst following the engine room. Rare earth metals, such as cerium (Ce) and lanthanum (La), added as a co-catalyst are also present on the entire surface. Zirconium (Zr) and aluminum (Al) are the main components of the catalyst support. The quantitative results are given in **Table 1**.

### 2.2 Preparation of the leachate from the spent automotive catalyst

Leaching from the spent automotive catalyst was inves-

**Fig. 4** Effects of various parameters on the dissolution efficiency of PGMs (2.5 g catalyst powder in 50 mL HCl): (A) HCl concentration (time = 24 h,  $T = 343$  K); (B) Leaching temperature (time = 24 h,  $[HCl]_{aq} = 5$  mol L<sup>-1</sup>); (C) Leaching time ( $[HCl]_{aq} = 5$  mol L<sup>-1</sup>,  $T = 343$  K)

tigated using HCl solution. PGMs are difficult to directly dissolve in acids, but they can be dissolved as a  $\leq 75$   $\mu$ m powder (Gurung *et al.*, 2013). The effect of the HCl concentration on the dissolution efficiencies of the PGMs is shown in **Figure 4A**. PGM dissolution increases with increasing HCl concentration, because dissolution of PGMs proceeds by chlorination of the metals. However, taking into account that the leachate is subjected to an extraction procedure, a feed solution with too high of HCl concentration is not favorable. Therefore, 5 mol L<sup>-1</sup> HCl was chosen as the leaching solution. Pd readily dissolves in HCl, but the dissolution efficiencies of Pt and Rh are lower than that of Pd. Thus, the leaching conditions were further optimized by investigating the effects of the leaching temperature and time. Dissolution of the PGMs increases with increasing leaching temperature (**Figure 4B**). However, PGM dissolution does not significantly improve at temperatures above 343 K. Increasing the leaching time is effective for PGM dissolution, since chlorination of PGMs is slow under current experimental conditions that do not use an oxidizer to accelerate the reaction. Extending the leaching time from 12 to 48 h significantly improves the degree of PGM dissolution (**Figure 4C**). Quantitative PGM dissolution can be achieved using 5 mol L<sup>-1</sup> HCl for 48 h operation at 343 K. The composition of the leachate is given in **Table 2**.

The results show that the spent automotive catalyst contains 5.3 g of PGMs/Kg catalyst, demonstrating that the spent automotive catalyst is a high grade ore compared with natural resources, such as pentlandite, pyrrhotite, and pyrite (Piña *et al.*, 2010). The leachate contains high concentrations of rare earth metals, such as Ce and La, and large amounts of common metals, such as Al and Mg, along with the PGMs.

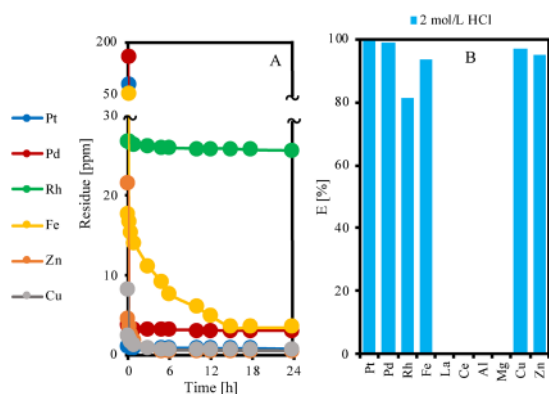


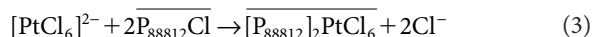
Fig. 5 (A) Effect of contact time on model leachate extraction ( $V_{\text{aq}}/V_{\text{IL}}=2$ ,  $[\text{HCl}]_{\text{aq}}=5 \text{ mol L}^{-1}$ ,  $T=298 \text{ K}$ ); (B) Data for extraction from the spent catalyst leachate using  $\text{P}_{8,8,8,12}\text{Cl}$  ( $V_{\text{aq}}/V_{\text{IL}}=2$ , time = 8 h,  $T=298 \text{ K}$ )

### 2.3 Extraction of the metal ions contained in the leachate

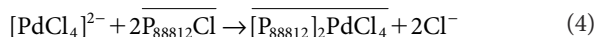
Among the PGMs in the leachate, Pt and Pd are readily separated from Rh using  $\text{P}_{8,8,8,12}\text{Cl}$  by changing the HCl concentration in the aqueous feed phase, as described in a previous paper (Firmansyah *et al.*, 2018). It has also been reported that quantitative extraction of Pd is achieved in a short time (Firmansyah *et al.*, 2019). Automotive waste catalysts contain a variety of metals depending on the type, model, and year of the car. Thus, the changes of the metal concentrations in the leachate ( $5 \text{ mol L}^{-1}$  HCl) with extraction time were measured (Figure 5). PGM ions are mainly present as metal-chloro complex anions in chloride environment as shown in the speciation diagrams (Figure S1), and they are extracted by electrostatic interaction with the cationic moieties of  $\text{P}_{8,8,8,12}\text{Cl}$  molecules.

The large amounts of Al and Mg in the leachate are not extracted at all. Rare earth metals are also not extracted. However, some metal ions such as Fe, Cu, and Zn which can form anionic complex under the current chloride ion concentration are extracted along with the PGMs.

The concentrations of Pt(IV) and Pd(II) rapidly decrease, and quantitative extraction is achieved within 10 min.  $[\text{PtCl}_6]^{2-}$  is the dominant Pt species in a wide HCl concentration range, which is supported by the ultraviolet (UV) spectrum of the aqueous phase (Figure S2). The extraction mechanism of Pt(IV) by  $\text{P}_{8,8,8,12}\text{Cl}$  is considered to be as given by Eq. (3).



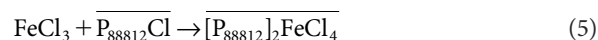
The extraction mechanism of Pd(II), whose dominant species under the present conditions is  $[\text{PdCl}_4]^{2-}$  from the UV spectrum (Figure S3), is likely to be anion exchange.



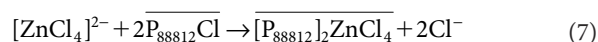
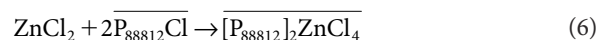
Herein, the horizontal bars denote the organic phases. Pd(II) has a significantly higher reaction rate than other metals (Funahashi, 1999). Deeth and Elding reported that

Pt(IV) also has a high reaction rate, although it has a slightly higher activation energy than Pd(II) (Deeth and Elding, 1996). The geometry of  $[\text{PdCl}_4]^{2-}$  also enhances the reactivity of Pd compared with other metals (Schumann and Elias, 1985). Thus, rapid extraction of Pt is also achieved, with quantitative extraction within 10 min. Fe, Cu, and Zn are simultaneously extracted with high efficiency along with Pt and Pd, although the extraction rates are slightly lower than those of Pt and Pd.

The metal-chloro complex species, which depends on the HCl concentration, determines the extraction mechanism. As reported in our previous study, extraction of  $\text{FeCl}_3$ , which is the dominant Fe species in the aqueous feed solution, occurs by ion association of the IL cation with  $[\text{FeCl}_4]^-$  (Firmansyah *et al.*, 2019).

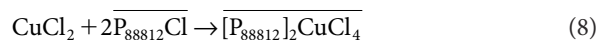


According to the literature (Gallardo *et al.*, 2008), extraction of Zn(II) from chloride solution can proceed by two different mechanisms depending on the HCl concentration, which are the ion association mechanism and the anion exchange mechanism given as Eqs. (6) and (7), respectively.



According to slope analysis, two molecules of  $\text{P}_{8,8,8,12}\text{Cl}$  are required to extract one divalent Zn(II) ion (Figure S4A). This is in agreement with the complex speciation diagram of Zn(II), which shows that  $[\text{ZnCl}_4]^{2-}$  is the dominant species in  $5 \text{ mol L}^{-1}$  HCl solution (Figure S1). Thus, extraction of Zn(II) is by the anion exchange mechanism (Eq. (7)).

For Cu(II),  $\text{CuCl}_2$  is dominant in a wide HCl concentration range based on the speciation diagram (Figure S1). The presence of  $\text{CuCl}_2$  in the HCl solution was confirmed by UV-visible (vis) spectroscopy, where an absorption band at 265 nm attributed to  $\text{CuCl}_2$  is present in the spectrum (Figure S4C) (Ong *et al.*, 2015). Extraction of Cu(II) might proceed by the ion association mechanism given as Eq. (8).



In slope analysis of an organic solvent system, two  $\text{P}_{8,8,8,12}\text{Cl}$  molecules are required to extract one Cu(II) ion (Figure S4B).

Rh extraction is significantly affected by the HCl concentration. The low extraction efficiency of Rh in Figure 5A can be attributed to the formation of  $[\text{RhCl}_6]^{3-}$  in the aqueous feed solution at high HCl concentration. Formation of the  $[\text{RhCl}_6]^{3-}$  complex with three  $\text{P}_{8,8,8,12}\text{Cl}$  molecules is difficult because the geometry has steric hindrance and high charge density (Firmansyah *et al.*, 2018). The tendency for chlorocomplexes to form ion pairs depends on the charge to size ratio or charge density (Bernardis *et al.*, 2005). In our previous study, extraction was achieved at below



3 mol L<sup>-1</sup> HCl, where [RhCl<sub>5</sub>]<sup>2-</sup> is the dominant Rh species in aqueous solution (Firmansyah *et al.*, 2019). Formation of the 1:2 complex of [RhCl<sub>5</sub>]<sup>2-</sup> with P<sub>8,8,8,12</sub>Cl is preferable under such conditions. However, aqua chlorocomplexes are known to be kinetically inert (Narita *et al.*, 2008), and [RhCl<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup>, that is, the complex in which one Cl of [RhCl<sub>6</sub>]<sup>3-</sup> is replaced by H<sub>2</sub>O is considered to be disadvantageous for the formation of the ion pair with IL cations. Thus, the extraction rate of Rh with P<sub>8,8,8,12</sub>Cl is slower than those of Pt and Pd. Thus, the extraction behavior of the metal ions in the raffinate after extracting Pt and Pd was investigated after adjusting the HCl concentration to 2 mol L<sup>-1</sup> (Figure 5B). Eighty percent of Rh is extracted to the IL phase, but impurity metals, such as Fe, Zn, and Cu, also move to the IL if they are contained in the raffinate.

## 2.4 Stripping of the metals from the IL phase

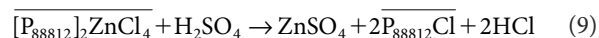
As described above, the leachate from spent automotive catalysts contains a variety of metals other than PGMs. Efficient recovery of the PGMs from the IL and removal of the impurity metals co-extracted with the PGMs are crucially important for PGM recycling. Therefore, the stripping performance of the metals from metal-loaded P<sub>8,8,8,12</sub>Cl using different stripping reagents was investigated. The results are given in **Table 3**.

Water is ineffective in stripping any of the metals from the IL because of the strong bonds between the IL cations and metal-chloro complexes. The absence of exchangeable anion species in water and the interface barrier may prevent the recovery of the metal-chloro complexes (Nguyen *et al.*, 2016).

In our previous study, we found that Fe(III) can be stripped from the P<sub>8,8,8,12</sub>Cl phase by reducing Fe(III) to Fe(II) using Na<sub>2</sub>SO<sub>3</sub> (Firmansyah *et al.*, 2019). About 90% of Fe can be removed from the metal-loaded IL phase by contact with 1.2 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> at 303 K, while Pt and Pd remain in the IL phase (Table 3).

NH<sub>4</sub>OH can quantitatively strip Zn and Cu, which have high affinity for P<sub>8,8,8,12</sub>Cl. However, a white precipitate is formed at the interface between the IL and the aqueous

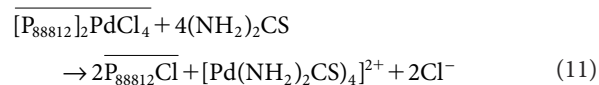
phase after the operation, which could limit the reusability of P<sub>8,8,8,12</sub>Cl. High stripping efficiencies of Zn and Cu are also achieved using 3 and 5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, where the efficiency increases with increasing acid concentration. However, removal of such metals using 5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> is accompanied by stripping of Pt and Pd. The stripping process is facilitated by formation of ZnSO<sub>4</sub> and CuSO<sub>4</sub>. The presence of ZnSO<sub>4</sub> in the stripping solution was confirmed by Fourier transform infrared (FTIR) spectroscopy, which shows ZnSO<sub>4</sub> signature peaks at 1194, 1150, and 1080 cm<sup>-1</sup> (**Figure S5A**). Thus, stripping of Zn from metal-loaded P<sub>8,8,8,12</sub>Cl most likely occurs by way of Eq. (9).



The stripping solution was then subjected to UV spectroscopy. The UV spectrum shows a major absorption band at 638 nm, which can be ascribed to the presence of CuSO<sub>4</sub> (**Figure S5B**) (Nakaoka and Ogura, 2002). Thus, stripping of Cu most probably occurs by way of Eq. (10).



Selective stripping of PGMs is essential for efficient PGM recovery. HNO<sub>3</sub> can recover a significant amount of Pt. Because other common co-extracted metals are not recovered, HNO<sub>3</sub> is considered to be a suitable recovery agent for Pt. As previously reported, CS(NH<sub>2</sub>)<sub>2</sub> shows good performance in quantitative stripping of Pd from metal-loaded P<sub>8,8,8,12</sub>Cl (Firmansyah *et al.*, 2019). The nature of Pd as a soft acid and CS(NH<sub>2</sub>)<sub>2</sub> as a soft base promotes formation of [Pd(CS(NH<sub>2</sub>)<sub>2</sub>)<sub>4</sub>]<sup>2+</sup>, which is supported by the UV spectrum of the stripping solution (**Figure S6**) (Sun and Lee 2011). Thus, Pd is stripped by the coordination-substitution reaction between CS(NH<sub>2</sub>)<sub>2</sub> and Cl<sup>-</sup> (Nguyen *et al.*, 2017).



**Table 3** Stripping of metals from loaded P<sub>8,8,8,12</sub>Cl with various stripping solutions

S [%]	Pt(IV)	Pd(II)	Rh(III)	Fe(III)	Cu(II)	Zn(II)
H <sub>2</sub> O	0	0	0	0	0	0
3 mol L <sup>-1</sup> HNO <sub>3</sub>	<b>58.4</b>	11.4	0	0	0	0
5 mol L <sup>-1</sup> HNO <sub>3</sub>	<b>82.1</b>	14.1	0	1.2	0	0
0.5 mol L <sup>-1</sup> NaClO <sub>4</sub>	<b>15.4</b>	1.0	0	0	0	0
1 mol L <sup>-1</sup> CS(NH <sub>2</sub> ) <sub>2</sub> in 1 mol L <sup>-1</sup> HCl	18.8	<b>86.6</b>	0	0	0	0
0.1 mol L <sup>-1</sup> CS(NH <sub>2</sub> ) <sub>2</sub> in 1 mol L <sup>-1</sup> HCl	10.1	<b>90.9</b>	0	0	0	0
0.1 mol L <sup>-1</sup> CS(NH <sub>2</sub> ) <sub>2</sub> in 0.5 mol L <sup>-1</sup> HCl	2.7	<b>88.6</b>	0	0	0	0
1.2 mol L <sup>-1</sup> Na <sub>2</sub> SO <sub>3</sub>	1.4	3.9	0	<b>90.2</b>	0	0
1 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	6.2	3.5	0	20.5	<b>66.4</b>	<b>73.9</b>
3 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	8.4	4.5	0	21.0	<b>83.5</b>	<b>82.7</b>
5 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	25.8	13.7	0	23.6	<b>88.4</b>	<b>83.3</b>
0.5 mol L <sup>-1</sup> NH <sub>4</sub> OH	0.2	15.7	0	0	<b>98.2</b>	<b>95.2</b>
5 mol L <sup>-1</sup> HCl*	0.3	0.1	<b>81.7</b>	7.8	0.1	0

\*Stripping after second extraction.

A mixture of HCl and CS(NH<sub>2</sub>)<sub>2</sub> has been used to strip Pt and Pd from different loaded organic phases (Sun and Lee, 2011, Lee *et al.*, 2010). When both Pt and Pd are present, substitution between CS(NH<sub>2</sub>)<sub>2</sub> and Cl<sup>-</sup> competitively occurs and depends on the concentration of the metal ion complexes (Swain *et al.*, 2010). Recovery of Pd with 1 mol L<sup>-1</sup> CS(NH<sub>2</sub>)<sub>2</sub> dissolved in 1 mol L<sup>-1</sup> HCl occurs with recovery of a significant amount of Pt (Table 3). Thus, the composition of CS(NH<sub>2</sub>)<sub>2</sub> and HCl was adjusted to minimize stripping of Pt. Decreasing the CS(NH<sub>2</sub>)<sub>2</sub> concentration from 1 to 0.1 mol L<sup>-1</sup> hardly affects Pd stripping, but stripping of Pt is significantly reduced (Table 3). Stripping of Pt can be further suppressed by adjusting the HCl concentration (Sun and Lee, 2011, Nguyen *et al.*, 2017). Pt is rarely stripped by decreasing the HCl concentration from 1 to 0.5 mol L<sup>-1</sup>, although the stripping efficiency of Pd slightly decreases.

In the competitive substitution reaction, Cl in the [P<sub>8,8,8,12</sub>]<sub>2</sub>PdCl<sub>4</sub> complex is substituted by CS(NH<sub>2</sub>)<sub>2</sub> faster than the Pt-CS(NH<sub>2</sub>)<sub>2</sub> complex (Swain *et al.*, 2010). Thus, Pd can be efficiently stripped at a low CS(NH<sub>2</sub>)<sub>2</sub> concentration, while stripping of Pt gradually increases as the CS(NH<sub>2</sub>)<sub>2</sub> concentration increases. Selective stripping of Rh from metal-loaded P<sub>8,8,8,12</sub>Cl can be achieved using 5 mol L<sup>-1</sup> HCl.

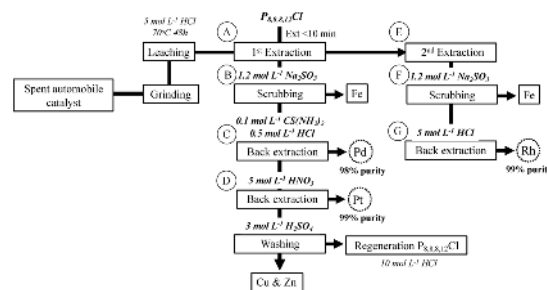
## 2.5 Recovery of the PGMs from the leachate of the spent automotive catalyst

Based on the extraction and stripping test results, the process for recovery of Pt, Pd, and Rh from the spent automotive catalyst leachate (5 mol L<sup>-1</sup> HCl) is shown in **Figure 6**. All of the extraction and stripping operations were performed at  $V_{aq}/V_{IL}=2$ . The metal concentrations in the solution after each process are given in **Table 4**. The leachate (Table 4, A) was directly mixed with P<sub>8,8,8,12</sub>Cl to allow for Pt and Pd extraction. After the first extraction stage, Pt and Pd are almost quantitatively extracted in 10 min, followed by Cu, Zn (approximately 90%), and Fe (approximately 65%) (Table 4, B).

The metal-loaded P<sub>8,8,8,12</sub>Cl was then moved to the scrubbing stage. Fe is almost completely removed from the IL

phase by operation for 30 min at 303 K using 1.2 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub> while leaving Pt and Pd in the IL (Table 4, C). Pd and then Pt are recovered from the IL using 0.1 mol L<sup>-1</sup> CS(NH<sub>2</sub>)<sub>2</sub> in 0.5 mol L<sup>-1</sup> HCl and 5 mol L<sup>-1</sup> HNO<sub>3</sub>, respectively. About 94% of Pd and 90% of Pt are selectively recovered from the IL phase, where the purities in the recovery solutions are >98% for both Pd and Pt (Table 4, D and E). After stripping Pd and Pt, the IL phase was washed with 3 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> to remove Cu and Zn. The raffinate of the first extraction stage with remaining Rh was subjected to a second extraction stage. The raffinate of 5 mol L<sup>-1</sup> HCl was diluted to 2 mol L<sup>-1</sup> HCl, followed by mixing with fresh P<sub>8,8,8,12</sub>Cl, resulting in 80% extraction of Rh (Table 4, F). After scrubbing with Na<sub>2</sub>SO<sub>3</sub>, the extraction IL phase (Table 4, G) was placed in contact with 5 mol L<sup>-1</sup> HCl for 24 h. About 80% of Rh is selectively recovered from the IL at 99% purity (Table 4, H). The final yields for Pt, Pd and Rh from the leachate are about 94%, 90% and 64%, respectively. For the Rh recovery, multi-stage operation is considered to be required.

Regeneration of P<sub>8,8,8,12</sub>Cl is possible using a high concentration HCl solution and the IL is reusable with minimal degradation in performance, as suggested by a previous study. Overall, P<sub>8,8,8,12</sub>Cl can selectively recover Pt, Pd, and Rh from the spent automotive catalyst leachate in high purities (approximately 99% for Pt and Pd).



**Fig. 6** Flow chart summarizing separation and recovery of PGMs from an automotive catalyst leachate

**Table 4** Metal concentrations in the respective phase after certain processes ( $V_{aq}/V_{IL}=2$ ,  $T=298$  K)

Step	Pt (mg/L)	Pd (mg/L)	Rb (mg/L)	Fe (mg/L)	Zu (mg/L)	Cu (mg/L)	Ce (mg/L)	La (mg/L)	Mg (mg/L)	Al (mg/L)
Initial conc.	78.7	156	26.8	50.2	21.6	8.2	399	523	1016	3792
A 1st extraction (in IL phase)	154	299	0	50.2	35.2	13.1	0.27	2.14	2	1.96
B Scrubbing (IL phase) <sup>a</sup>	153	298	0	2.36	35.2	13.1	0.27	2.13	2	1.96
C CS(NH <sub>2</sub> ) <sub>2</sub> (Pb stripping) <sup>b</sup>	2.14	140	0	0	0	0	0	0	0	0
D HNO <sub>3</sub> (Pb stripping) <sup>c</sup>	67.1	0.2	0	0	0	0	0	0	0	0
E 2nd extraction (IL phase) <sup>*</sup>	0.02	0.08	15.1	14	0	0	0.57	0.30	0.12	0.64
F Scrubbing (IL phase) <sup>a</sup>	0	0	15.1	1.36	0	0	0	0	0	0
G HCl (Rh stripping) <sup>d</sup>	0	0	6.81	0	0	0	0	0	0	0

<sup>\*</sup>Diluted from 5 to 2 mol L<sup>-1</sup>

<sup>a</sup>1.2 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>3</sub>, 303 K, 30 min

<sup>b</sup>0.1 mol L<sup>-1</sup> CS(NH<sub>2</sub>)<sub>2</sub> in 0.5 mol L<sup>-1</sup> HCl

<sup>c</sup>5 mol L<sup>-1</sup> HNO<sub>3</sub>

<sup>d</sup>5 mol L<sup>-1</sup> HCl.

## Conclusion

A hydrometallurgical process for the separation and recovery of PGMs from the leachate of spent automotive catalysts has been developed based on solvent extraction using the  $P_{8,8,8,12}Cl$  IL, which we recently developed as an extraction solvent for PGMs. The phosphonium-based IL extracts both Pt and Pd in high efficiency. In addition, selective recovery of Pt and Pd, which are usually difficult to separate, is achieved by a stripping process. Pt is selectively recovered using high concentration nitric acid, while Pd is recovered with thiourea in low concentration hydrochloric acid. Rh is extracted from the raffinate to  $P_{8,8,8,12}Cl$  after removing Pt and Pd in the first extraction stage, and then recovered by high concentration hydrochloric acid solution. Some common metals co-extracted into  $P_{8,8,8,12}Cl$  can be removed by using an effective stripping reagent for each metal. The results demonstrate the potential of well-designed ILs as extraction solvents for recycling valuable metals, such as PGMs, from waste products, which will contribute to solving environmental issues.

## Supplementary Information

Supplementary Information is available at <http://www.scej.org/publication/jcej/suppl/>

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