Effect of Hydrophobicity of Ionic Liquids on the Leaching Selectivity of Platinum from a Spent Automotive Catalyst

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Recycling platinum group metals from secondary resources such as spent automotive exhaust catalysts is promising for the circular economy. However, the selective separation of Pt over massive amounts of impurity metals such as Mg and Al is particularly challenging. In this study, non-aqueous direct leaching of platinum from a spent automotive catalyst (SAC) using hydrophobic ionic liquids, namely, trihexyl(tetradecyl)phosphonium chloride ($P_{66614}Cl$) and trioctyl(dodecyl)phosphonium chloride ($P_{88812}Cl$) with the aid of pre-loading hydrochloric acid/hydrogen peroxide was proposed. The more hydrophobic $P_{88812}Cl$ exhibited more efficient and selective leaching of Pt over Mg and Al. The recovery of Pt from the metal-loaded $P_{88812}Cl$, and the reusability of the IL for SAC leaching were also demonstrated.

1. Introduction

Platinum group metals (PGMs) are of great interest owing to their high stability and catalytic activity. Especially platinum (Pt), palladium (Pd), and rhodium (Rh) play a vital role as the main catalytic component of automotive exhaust catalysts in catalytic converters [1]. Due to their limited reserves and uneven distribution of PGM resources, increasing the end-of-life recycling rate in various regions is essential for the stable supply of PGMs [2]. Even if electric vehicles become more popular and gasoline-powered vehicles become less common; PGM recycling will be increasingly requested owing to their demand in power source sectors such as fuel cells and electrolyzers [3].

Commercial SAC recycling has been operated by pyrometallurgy as the pretreatment for the solubilization of inert PGMs [4]. However, the massive energy consumption of pyrometallurgy (typically operated at temperatures higher than 1300 K) has been a great concern from an economic standpoint. The hydrometallurgical recycling of SACs has attracted wide attention owing to its lower energy consumption and process scalability [5]. The PGMs in SACs could be leached out along with other metals comprising the catalyst support by using highly acidic aqueous solutions such as aqua regia or inorganic acids with oxidants [6]. Subsequently, the dissolved PGMs could be separated from other impurity metals by solvent extraction. However, the consumption of inorganic acids for the leaching of automotive catalysts causes environmentally impactful acidic wastewater containing heavy metals. Moreover, solvent extraction for metal separation uses volatile organic solvents.

For more environmentally friendly recycling of SACs, the leaching and separation of PGMs without inorganic acids and organic solvents should occur. Solvometallurgy or Ionometallurgy has attracted attention in this context. These new concepts of metallurgy employ non-aqueous or less-aqueous media containing organic solvents, ionic liquids (ILs), and deep eutectic solvents as the alternative to conventional inorganic acids and organic solvents for lower emission processes [7,8]. Notably, water-immiscible hydrophobic solvents for leaching provide an advantage that the leached metals can be easily recovered by contacting with the aqueous stripping solution. Moreover, the solvent can be repeatedly used for metal processing. Wellens and colleagues reported the use of an acid-saturated hydrophobic ionic liquid for the leaching of metal oxides and also investigated the stripping behavior of the leached metals [9]. Li and colleagues reported that a trichloride hydrophobic ionic liquid could be reused after the leaching of a neodymium permanent magnet and stripping of the metals [10]. Non-aqueous direct leaching has been utilized for the leaching of SACs. Serpe and colleagues reported the leaching of Pd from a SAC using an organic ligand containing sulfur and iodine in organic solvents [11,12]. Nguyen and co-workers used acetonitrile with some metal salts as oxidants for the selective leaching of palladium and platinum from a SAC [13]. Li and co-workers reported the use of trihalide ILs for the selective leaching of palladium from a SAC. Lanaridi and co-workers used deep eutectic solvents for the leaching of a SAC [14]. The leaching of metals into organic solvents allows for advanced metal separation that is difficult to achieve in aqueous systems [15]. The non-aqueous leaching of PGMs from SACs presents advantages such as suppressing the leaching of Al, Mg, and other impurity metals from the catalyst support and improving the leaching selectivity. ILs could be utilized for the extraction and even non-aqueous direct leaching owing to their high affinity to PGMs [16]. The non-volatile feature of ILs realized a more environmentally friendly recycling process than using organic solvents. However, due to the lack of a systematic study of the structure of ILs on the leaching performance of metals from primary or secondary metal resources, the molecular design rule of the ILs has not yet been revealed.

In this study, we focused on revealing the molecular structure of the hydrophobic ILs on the leaching behavior of platinum from a SAC. Two phosphonium-based ILs trihexyl- (tetradecyl)phosphonium chloride ($P_{66614}Cl$) and trioctyl(dodecyl)phosphonium chloride ($P_{88812}Cl$) were employed as leaching media for the SAC. These ILs have already been reported as efficient extractants for PGMs. The acid/oxidant-saturating treatment was applied by contacting with hydrochloric acid (HCl)/hydrogen peroxide (H_2O_2) solution for these ILs to enhance the leaching. Finally, the separation and recovery of Pt from the metal-loaded IL were studied, and the reusability of the IL as the leaching medium was demonstrated.

2. Experimental

2.1 Reagents

The ILs, $P_{66614}Cl$ and $P_{88812}Cl$ were purchased from Sigma-Aldrich and Io-li-tec, respectively, with a purity of 95% each, and were used without further purification. The chemical structure of the ILs used in this study is shown in Figure 1. According to the previous literature, $P_{88812}Cl$ has a higher hydrophobicity owing to its larger carbon number, as evidenced by the minimum leakage of the phosphonium cation into the water phase [17]. Hydrochloric acid (10 mol/L) was purchased from Kishida Chemical. Hydrogen peroxide, ammonium chloride, and ICP standard solution of Pt, Fe, Zn, La, Al, and Mg were purchased

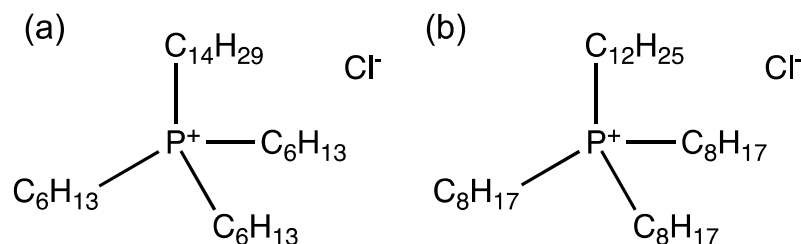from Fujifilm-Wako Chemical. Milli-Q water was used to prepare all the aqueous solutions.

Figure 1. Chemical structures of (a) $P_{66614}Cl$ and (b) $P_{88812}Cl$.

2.2 Direct leaching of a spent automotive catalyst by ILs

The ILs used in this study did not leach any metals from the SAC when used untreated. Therefore, a known concentration of HCl/H$_2$O$_2$ solution was contacted with the IL by vortex mixing at room temperature for 1 h to load acid/oxidant into ILs. The acid-loaded IL was then added to the SAC and heated up to 343 K with stirring at 400 rpm for 24 h. The resulting leachate was centrifuged at 18,000g to obtain the supernatant. As a comparison, conventional aqueous leaching using HCl/H$_2$O$_2$ was also conducted by following a similar protocol according to the previous literature [18]. The metal concentration in the IL was directly measured by an inductively coupled plasma optical emission spectrometer (Optima 8300, Perkin-Elmer) equipping a 1 mm diameter injector and a torch for organic solvent with a Perche-cooler chamber. The sample solution was prepared as matrix-matched in 20% aqueous components in ethanol. The calibration score of this organic system was $R^2 > 0.999$, showing good linearity. The leaching efficiency (%L) was evaluated by the following equation:

$$\%L = \frac{C_{M,leaching} \times V}{m_M / w} \times 100 \tag{1}$$

where $C_{M,leaching}$, V, m_M, and w represent the metal concentration of a metal M in the IL phase, volume of IL, mass ratio of M, and the weight of the SAC, respectively.

2.3 Stripping of metals from $P_{88812}Cl$ after SAC leaching

The stripping of the metals from the IL after leaching was performed by contacting various aqueous solutions with the IL at an aqueous-to-organic (A/O) ratio of 5/1 at room temperature by vortex mixing. The stripping percentage (%S) was evaluated by the following equation:

$$\%S = \frac{C_{M,stripping}}{C_{M,leaching}} \times 100 \tag{2}$$

where $C_{M,stripping}$ represents the metal concentration in the IL phase after stripping.

3. Results and Discussion

3.1 Direct leaching of a spent automotive catalyst by ILs

The metal contents in the SAC used in this study are shown in Table 1. Due to the shallow content of Pd, it was not easy to quantify the metal content in the IL after leaching. Therefore, the rich metals in the SAC were featured for further leaching experiments. The leaching behavior of metals from the SAC by an aqueous solution of 5 mol/L HCl with 5% H$_2$O$_2$ and the ILs loaded with 5 mol/L HCl with 5% H$_2$O$_2$ is

shown in Figure 2. When an aqueous HCl/H$_2$O$_2$ solution was used for leaching, almost all the metals were efficiently dissolved, which means the leaching selectivity of Pt was very low. On the contrary, the SAC leaching with HCl/H$_2$O$_2$-loaded ILs could selectively dissolve Pt. The leaching of Mg and Al that were in large quantities in the SAC was significantly suppressed by IL-based leaching. The leaching mechanism for Pt was presumed to be different in the aqueous and the IL-based leaching. In the aqueous system, Pt was oxidized by Cl$_2$ which was produced from the reaction between HCl and H$_2$O$_2$ [18]. A comparable reaction may take place in the IL-based system, where HCl and H$_2$O$_2$ are dissolved at the pre-loading. Additionally, the Cl$_2$ gas generated in the aqueous HCl/H$_2$O$_2$ solution during the pre-loading could dissolve in the IL, forming trichloride anions which exhibit reactivity towards the oxidation of precious metals [19]. Comparing P$_{66614}$Cl and P$_{88812}$Cl, the latter performed better leaching performance for Pt with less leaching of Mg and Al. The suppression in the leaching of Mg and Al is very beneficial for the purification complexity of Pt after leaching. The higher leaching efficiency of Pt of P$_{88812}$Cl could be explained by the unintentional consumption of HCl/H$_2$O$_2$ for Al leaching: a higher %L of Al, presented in much larger quantities than Pt, was observed for P$_{66614}$Cl. P$_{88812}$Cl has more carbon and thus has a higher hydrophobicity. Therefore, the hydrophobicity of ILs might be a key to the selective leaching of Pt from the SAC.

Table 1. The metal contents in the SAC were determined by the leaching with aqua regia at a solid-to-liquid ratio of 12.5 g/L, 353 K for 24 h. The bold elements were featured for further leaching experiments.

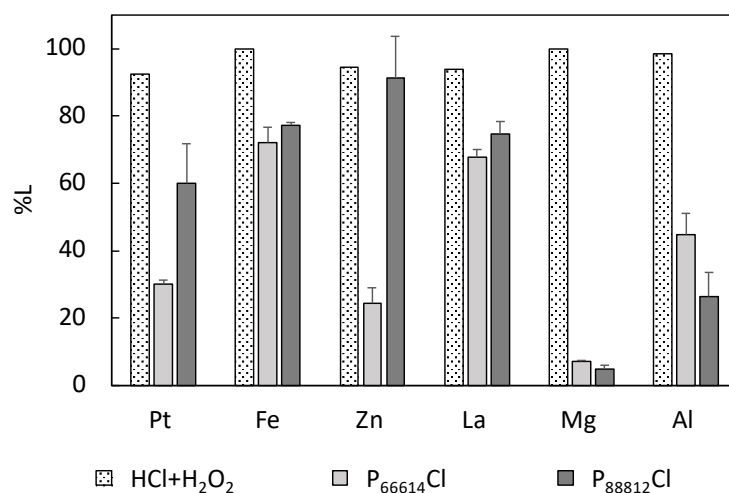| **Pt**	Pd	**Fe**	**Zn**	Cu	Ce	**La**	Zr	**Mg**	**Al**	Ba	Pr
4.1	1.4	**21.4**	**4.3**	0.3	13.2	**26.4**	1.2	**43.8**	**166.7**	32.7	13.5

Figure 2. Leaching of various metals from the SAC into various leaching solvents. The error bars on P$_{66614}$Cl and P$_{88812}$Cl are standard deviations.

The affinity of the metal ions with the ILs is essential to the leaching selectivity of metals into ILs. The liquid-liquid extraction behavior of metals with the ILs that could be an indicator of metal-IL affinity is shown in Figure 3. It was obvious that P$_{66614}$Cl and P$_{88812}$Cl have a similar extraction performance: Pt, Fe, and Zn were efficiently extracted in the wide range of HCl concentrations. La and Al were very slightly

extracted in $P_{66614}Cl$, and were not extracted in $P_{88812}Cl$. Mg was not extracted in either IL. These ILs have a higher affinity towards Pt, Fe, and Zn, which likely form anionic chloro-complexes in the chloride media, while they have a low affinity for La, Mg, and Al which are bare cations. A similar extraction selectivity of ILs to these metals from SAC leaching solutions was reported in the literature [20-23]. Therefore, it was indicated that the leaching selectivity for ILs observed in Figure 1 followed the affinity of the leached metals for ILs.
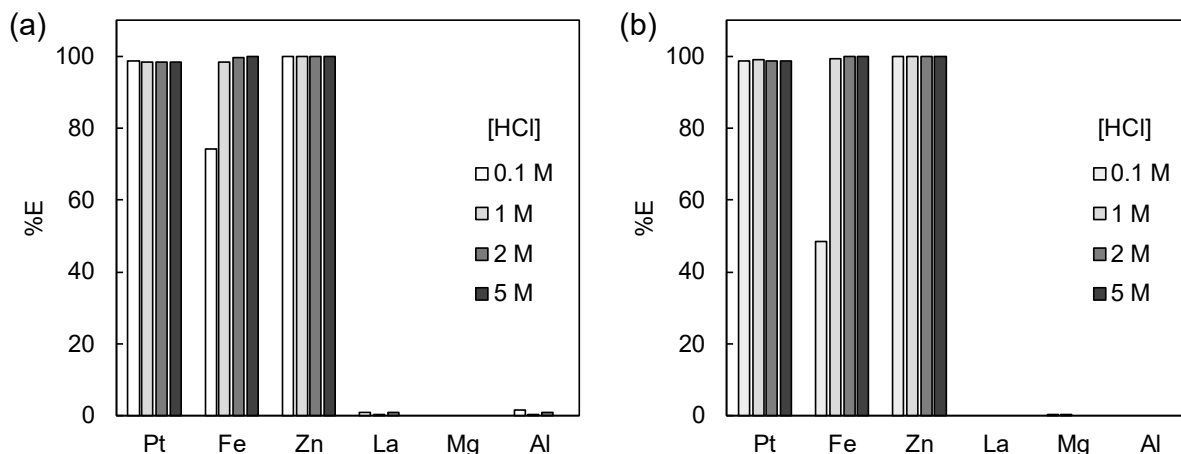

Figure 3. Liquid-liquid extraction of Pt(IV), Fe(III), Zn(II), La(III). Mg(II), and Al(III) from various HCl concentrations by (a) $P_{66614}Cl$ and (b) $P_{88812}Cl$.

To further investigate the effect of the hydrophobicity of IL on the leaching selectivity, the water content of the ILs after contact with the HCl/H_2O_2 solution was measured. It is assumed that the loading of HCl and H_2O_2 into the IL through pre-loading is accompanied by the water molecules. Hence, the water content of the ILs can serve as an indicator of the loading amount of HCl and H_2O_2. As shown in Figure 4, the water content in $P_{66614}Cl$ tended to increase with the increase of HCl concentration in the aqueous phase, while that in $P_{88812}Cl$ was lesser, and was constant even with varied HCl concentrations.
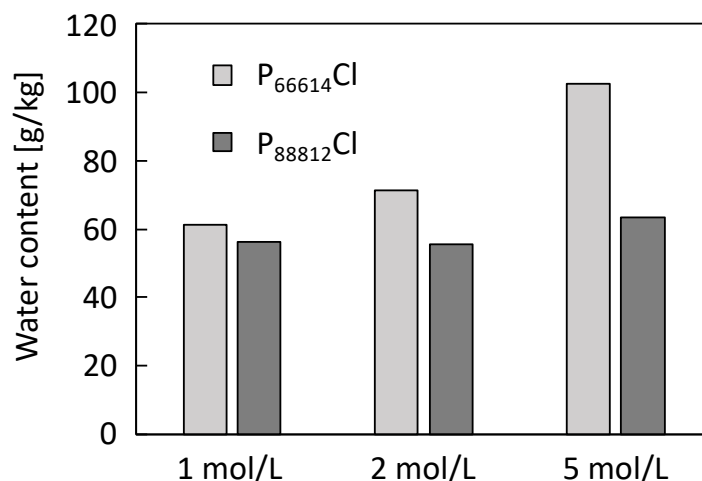

Figure 4. The water content of ILs after loading HCl/5%-H_2O_2 solution with different HCl concentrations measured by Karl-Fisher titration. Each titration was triplicated.

The effect of the HCl concentration in the loading HCl/H_2O_2 solution on the leaching efficiency of the metals from the SAC using ILs is shown in Figure 5. Interestingly, the %L of Pt and Al into P_{66614}Cl was almost independent of the loading HCl concentration, while the leaching of Fe and La gradually increased with increasing the HCl concentration. This could be attributed to the increase of H_2O loading in the IL, leading to the undesired leaching of impurity metals such as Fe and La. For P_{88812}Cl, Pt leaching was significantly improved when the loading HCl concentration was as high as 5 mol/L, while the leaching of Mg and Al was kept low. This suggests that the primary active species for Pt leaching in P_{88812}Cl was not HCl/H_2O_2 but trichloride anions without unavoidable H_2O loading at a high concentration of pre-loading HCl.
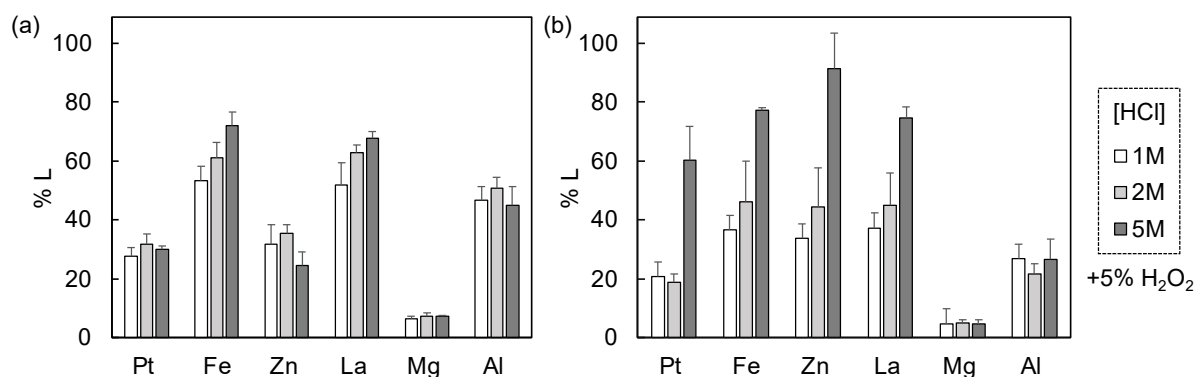

Figure 5. Effect of loading HCl concentration on the leaching efficiency of metals from the SAC using (a) P_{66614}Cl and (b) P_{88812}Cl as leaching solvents. The error bars are standard deviations.

3.2 Recovery of Pt from the metal-loaded P_{88812}Cl

After the SAC leaching with P_{88812}Cl, the IL phase contained Pt with some impurity metals. Therefore, the scrubbing and stripping of metals from the IL phase were studied to recover Pt. According to our preliminary investigation, it was suggested that the use of Na_2SO_3 with the addition of NH_3 could be used for the removal of impurity metals such as Fe, La, Mg, and Al, while HNO_3 for the stripping of Pt. The effect of contact time on the stripping of various metals from P_{88812}Cl after SAC leaching using Na_2SO_3 is shown in Figure 6a. The removal of La, Mg, and Al was easily achieved at any contact time, while Fe removal required a contact time longer than 2 h. This is because of the stripping mechanism of Fe by Na_2SO_3: Fe(III) was reduced to Fe(II) by Na_2SO_3 to deform the extractable anionic chloro-complex. However, the re-extraction of Zn(II) occurred with time probably due to the increase of Cl^- concentration in the stripping solution. The effect of the A/O ratio on the stripping of metals using 5 M HNO_3 is shown in Figure 6b. The stripping efficiency of Pt was improved by increasing the A/O ratio from 1:1 to 3:1. Therefore, the scrubbing of impurity metals and the stripping of Pt could be done by using Na_2SO_3 and HNO_3 at the optimized conditions.
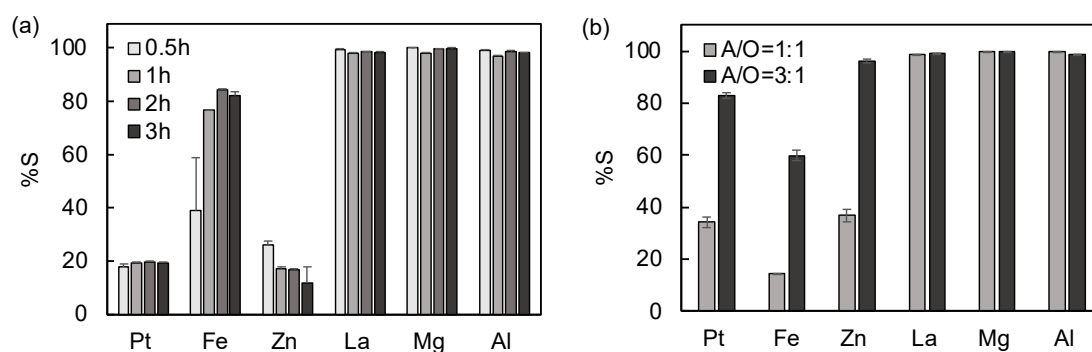
Figure 6. Stripping behavior of various metals from $P_{88812}Cl$ after the SAC leaching, (a) effect of contact time of 0.5 mol/L Na_2SO_3 (with 0.5 mol/L NH_3) on the removal of impurity metals, A/O=1:1, vortex at room temperature, and (b) effect of A/O ratio of 5 mol/L HNO_3 on Pt stripping, vortex for 1 h at room temperature.

3.3 Stability and reusability of IL

After the scrubbing and stripping of metals from the metal-loaded $P_{88812}Cl$, the IL could be further utilized for the SAC leaching. To ensure the chemical stability of the IL, ^{31}P-NMR of the IL before and after the SAC leaching was measured. As shown in Figure 7a, there was almost no change in the spectra before and after the leaching, indicating the IL has high chemical stability even under a strongly oxidative condition. After the 1st leaching, scrubbing, and stripping, the IL was used for the SAC leaching again and the leaching performance was investigated, as shown in Figure 7b. The leaching behavior of metals from the SAC using the reused $P_{88812}Cl$ was almost the same trend as the 1st leaching. The high stability and reusability of the IL were demonstrated.
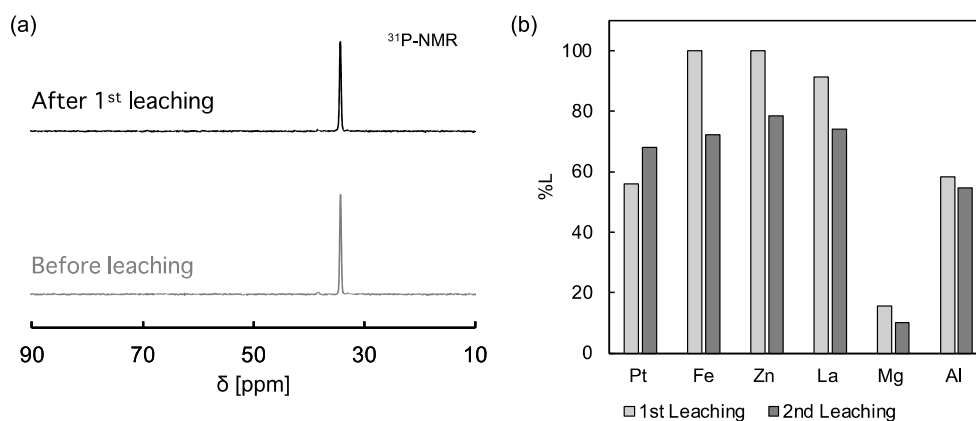

Figure 7. The stability and reusability studies of IL, (a) ^{31}P-NMR spectra of the $P_{88812}Cl$ before and after the SAC leaching, and (b) comparison of the 1st and 2nd SAC leaching performance using $P_{88812}Cl$.

4. Conclusion

In this study, two hydrophobic ILs with different alkyl chain lengths, namely, $P_{66614}Cl$ and $P_{88812}Cl$, were used for non-aqueous direct leaching of PGMs from a SAC. Interestingly, more hydrophobic IL $P_{88812}Cl$ performed more efficient and selective leaching of Pt compared to $P_{66614}Cl$. This might occur since

the $P_{66614}Cl$ underwent an undesired consumption of loaded HCl/H_2O_2 to the leaching of the impurity metals such as Al. The scrubbing and stripping from the metal-loaded $P_{88812}Cl$ allowed the separation and recovery of Pt from other impurity metals, and the IL could be reused for multiple leaching cycles. The results of this study indicate that ILs of higher hydrophobicity, which contains less water and high acid/oxidant during the loading of the aqueous acid/oxidant solution, is advantageous for the selective leaching of Pt. Further PGM selective leaching from SACs will be possible by discovering a method that allows loading acid/oxidant into ILs while preventing water contamination.

Acknowledgment

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