Leaching of Pt, Pd and Rh from Automotive Catalyst Residue in Various Chloride Based Solutions

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Platinum-group metals (PGM) are important precious metals in many industrial fields. However, their natural resource deposits are strictly limited. Accordingly, their recycling process from wastes and/or secondary resources must be considered. In this study, the leaching of PGM from automotive catalyst residue was performed based on the formation of their chloro-complexes in various concentration of acidic solution. The recovery of platinum, palladium and rhodium from the samples after hydrogen reduction pretreatments was examined in the leaching process by using a mild solution mixture of NaClO–HCl and H_2O_2 at 65°C for 3 h. Effect of other solution mixtures on the extraction of the precious metals was also compared with NaClO–HCl–H₂O₂, such as HCl–H₂O₂ and NaClO–HCl. The optimum condition to dissolve platinum, palladium and rhodium was achieved by the mixture of 3 vol% NaClO, 5 kmol·m⁻³ HCl and addition of 1 vol% H₂O₂. The recovery of platinum, palladium and rhodium after 3 h leaching reaches 88%, 99%, 77%, respectively.

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1. Introduction

Platinum-group metals (PGM) are important precious metals in many industrial fields, for instance catalyst materials, especially as an automotive catalyst. The development and commercial application of the catalytic control for automotive exhaust has increased worldwide for decades, as a concern of environmental protection from major air pollution. Three-way catalyst (TWC) is an advanced automotive catalyst which can reduce more than 99% of emissions. It responds to the demands of simultaneously catalyzing the reactions, such as CO oxidation, hydrocarbon oxidation and NO_x reduction.¹⁻³⁾ Three metals of platinum group metals (PGM), i.e. platinum (Pt), palladium (Pd) and rhodium (Rh) are employed as active materials in TWC. Their natural resource deposits are strictly limited. Accordingly, their recycling process from wastes and/or secondary resources such as spent automotive catalyst or residue must be considered. The reasons are not only justified for cost saving and materials utilization efficiency but also sustainable utilization of natural resources.

Typically, hydrometallurgical process is selected to recycle PGM through leaching process. In general, PGM dissolve in aqua regia and mineral acids, such as hydrochloric acid, nitric acid and sulfuric acid. To some extent, PGM could be leached in a relatively low concentration of acid.⁴⁾ Pd was dissolved completely by using NaClO, NaCl at pH 1.2. Sulfuric acid (60%) with NaCl addition was applied to leach Pt, Pd and Rh from nitric acid manufacture catalyst which contained nitric oxide at a temperature of $135^{\circ}C^{.5}$. After 10 h leaching, about 99% of PGM was dissolved.

In the case of automotive catalyst recycling, the presence of Pt, Pd, Rh and other supporting oxides makes the leaching process more complex. Several studies had been made to leach PGM from new or spent automotive catalyst with higher extraction efficiency. Leaching of Pt and Rh from spent honeycomb catalyst had been conducted by using a boiling solution containing 8 kmol·m⁻³ HCl and 3.5 kmol· m⁻³ HNO₃ with the addition of AlCl₃.⁶⁾ The leaching process dissolved Pt and Rh about 95 and 82%, respectively. Rh dissolution was raised slightly by replacing a part of the HCl with AlCl₃ with the addition up to $0.8 \text{ kmol} \cdot \text{m}^{-3}$. In another study, PGM in new and spent automotive catalyst were extracted by using raw HCl $(12 \text{ kmol} \cdot \text{m}^{-3})$ and H₂SO₄ with the addition of fluoride ions and H_2O_2 either periodically or continously.⁷⁾ A pretreatment process was undertaken before leaching by using H₂SO₄, sodium borohydrate and H₂ gas. The results showed that the best extraction ratios of Pt, Pd and Rh were 96, 98 and 99%, respectively. Another procedure to recover Pt and Rh from spent automobile catalyst was also developed.⁸⁾ The procedure consisted of reduction leaching (H₂SO₄ and N₂H₆SO₄), oxidation leaching (NaClO, HCl and AlCl₃), final leaching (HCl) and neutralization (metallic Al). The integrated procedure gave the recovery of Pt and Rh about 94 and 89%, respectively.

In this study, PGM (Pt, Pd and Rh) from an automobile catalyst residue were attempted to be recycled with relatively higher efficiency by using chloride based leaching solution simultaneously. One-step leaching was applied to simplify the leaching process using a solution which consisted of HCl and H_2O_2 . Then, the usage of HCl in the leaching solution was partly substituted by NaClO. The substitution of Cl ion supplier from HCl to NaClO aims to obtain the leaching

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solution with lower acidity without changing the dissolution efficiency of PGM.

2. Theoretical Background

Pt, Pd and Rh have great capacity to form halo-complexes in halide solution with high acidity. Pt is mainly present in the II and IV oxidation state. In the chloride solution, chlorocomplexes of Pt are formed with coordination numbers 4 and 6 for II and IV oxidation states, respectively. In the case of Pd, the oxidation states II and IV are taken up in solid compounds. The chloro-complexes of Pd appear with the coordination numbers 4 and 6 for II and IV oxidation states, respectively. The most stable oxidation state of Rh is in the III oxidation state. Rh has a great tendency to form complex ions with coordination number 6.⁹

Some chemical reactions involving Pt, Pd and Rh in HCl– H_2O_2 and NaClO–HCl system are described below.^{9,10)} For HCl– H_2O_2 system, the following reactions may take place. Main reaction:

$$Pd + H_2O_2 + 4HCl \leftrightarrow H_2PdCl_4 + 2H_2O$$
(1)

Anodic: $Pd + 4Cl^- \leftrightarrow PdCl_4^{2-} + 2e$ $E^o = -0.62 V$ Cathodic: $H_2O_2 + 2H^+ + 2e \leftrightarrow 2H_2O$ $E^o = 1.76 V$ H_2O_2 can easily react with HCl to form Cl₂ and water.

$$H_2O_2 + 2HCl \leftrightarrow Cl_2 + 2H_2O$$
 $\Delta E = 0.51 V$ (2)

Thus, the formed active components, *i.e.* Cl₂, in the solution can also react with Pd through the following reactions.

$$Pd + 2HCl + Cl_2(aq) \leftrightarrow H_2PdCl_4$$
 (3)

Anodic:
$$Pd + 4Cl^{-} \leftrightarrow PdCl_{4}^{2-} + 2e$$

 $E^{o} = -0.62 V$
Cathodic: $Cl_{2}(aq) + 2e \leftrightarrow 2Cl^{-}(aq)$
 $E^{o} = 1.396 V$

The following reaction might also take place:

Pd + HClO + 3HCl
$$\leftrightarrow$$
 H₂PdCl₄ + H₂O (4)
Anodic: Pd + 4Cl⁻ \leftrightarrow PdCl₄²⁻ + 2e
 $E^{\circ} = -0.62 \text{ V}$
Cethodic: HClO + 2H⁺ + 2e \leftrightarrow Cl₂(g) + 2H₂O

Cathodic: HClO + 2H⁺ + 2e
$$\leftrightarrow$$
 Cl₂(g) + 2H₂O
 $E^{0} = 1.63 \text{ V}$

Analogous reactions can be respectively deduced for Pt and Rh when considering the following electrode reactions:

$$Pt + 6Cl^{-} \leftrightarrow PtCl_{6}^{2-} + 4e \qquad E^{0} = -0.744 V \quad (5)$$

$$Rh + 6Cl^{-} \leftrightarrow RhCl_{6}^{3-} + 3e \qquad E^{0} = -0.45 V \quad (6)$$

For the NaClO-HCl system, the following reaction will take place.

$$NaClO + HCl \leftrightarrow HClO + NaCl$$
 (7)

A reaction governing the Pd leaching is likely to occur:

$$Pd + HClO + 3HCl \leftrightarrow H_2PdCl_4 + H_2O$$
(8)

Anodic:
$$Pd + 4Cl^{-} \leftrightarrow PdCl_{4}^{2-} + 2e$$

 $E^{0} = -0.62 V$
Cathodic: $HClO + 2H^{+} + 2e \leftrightarrow Cl_{2}(g) + 2H_{2}O$

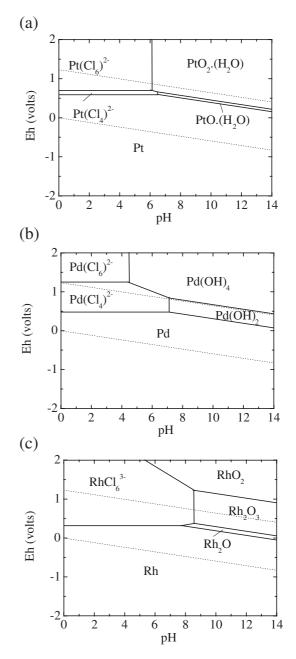


Fig. 1 Eh–pH diagram of (a) Pt–Cl–H₂O, (b) Pd–Cl–H₂O and (c) Rh–Cl–H₂O systems at the condition of metal concentration of 10^{-2} kmol·m⁻³, Cl concentration 5 kmol·m⁻³ and temperature at 25°C.

$E^{\rm o} = 1.63 \, {\rm V}$

Considering the equilibrium between Cl_2 and HClO in HCl solution: $Cl_2(aq) + H_2O \leftrightarrow HClO + HCl$; the following reaction might also take place:

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$$Pd + 2HCl + Cl_2(aq) \leftrightarrow H_2PdCl_4$$
 (9)

Anodic:
$$Pd + 4Cl^{-} \leftrightarrow PdCl_{4}^{2-} + 2e$$

 $E^{\circ} = -0.62 V$
Cathodic: $Cl_{2}(aq) + 2e \leftrightarrow 2Cl^{-}(aq)$
 $E^{\circ} = 1.396 V$

Analogous mechanism can be respectively expanded to Pt and Rh when considering the electrode reactions of (5) and (6).

The Eh–pH diagrams of Pt–Cl–H₂O, Pd–Cl–H₂O and Rh– Cl–H₂O systems are shown in Fig. 1, calculated based on available data in some literatures.^{9–11)} The chloro-complexes of Pt, Pd and Rh ions appear lying in the water stability regions, as shown in Figs. 1(a), (b) and (c). RhCl₆^{3–} occupies wider area in the diagram as compared with $PtCl_6^{2-}$ or $PdCl_6^{2-}$. The dissolution of Pt and Pd to their chlorocomplexes is limited by the occurrence of hydroxide of Pd and oxide-hydrate of Pt at neutral-basic area with high potential. Additionally, the formation of rhodium oxides seems to be easy in the area with relatively lower potential. The formation of rhodium oxides was also suggested to be the main obstacle to obtain higher Rh dissolution during PGM leaching, because rhodium oxides are almost insoluble in chloride solutions if without a powerful oxidizing agent.¹⁰)

3. Experimental Method

The automotive catalyst residue containing PGM was supplied by Cataler, Co. The received sample was pellet, which was pre-treated by means of hydrogen reduction (PR). Then, the sample was ground and sieved. The powder with a size of less than $500 \,\mu\text{m}$ ($-500 \,\mu\text{m}$) was used in the present experiments. The purpose was to make it more homogenous during the sampling and make it easier to agitate during the leaching. The powder sample was kept in a desiccator to avoid contamination. The PGM composition of the powders is listed in Table 1. The sample also contained about 90 mass% of support materials such as Al₂O₃, CeO₂, ZrO₂, BaO and other oxides. The reagents used in the experiments were NaClO solution (8.5-13.5% active chlorine, Nacalai tesque), HCl $(35-37\% = 12 \text{ kmol} \cdot \text{m}^{-3})$, Nacalai tesque) and H_2O_2 (30%, Nacalai tesque). Bi-distilled water was used for rinsing, washing and dilluting the solution in all experiments.

The leaching solutions were prepared in a 100 mL beaker. During the leaching experiments, a glass stopper was put on the top of the beaker glass freely, without changing the pressure in the beaker glass from atmospheric pressure. From several preliminary experiments, a leaching condition was determined and used as a default condition. Based on the default condition, the leaching experiments were conducted at 65°C for 3 h and agitated by a magnetic stirrer. Ratio of solid to liquid (pulp density) during the leaching was 500 g/L. This pulp density was employed to the experiments with the consideration of economic reason as required in industrial application.

Further, various chloride based leaching solutions were examined. At first, a raw solution of HCl ($12 \text{ kmol} \cdot \text{m}^{-3}$) was used in the leaching. Then, H₂O₂ was added to HCl based leaching solution. The concentration of HCl was varied and

 Table 1
 Composition of PGM analyzed by ICP (wet-analysis) after alkali leaching.

Elements	[PR] (mass%)
Pt	0.379
Pd	0.582
Rh	0.239

examined in the leaching process. In the next step, NaClO was introduced in the leaching solution to substitute the Cl ion supplier from HCl, partially. The concentration of NaClO and H_2O_2 was also varied to obtain the optimum condition. The leaching conditions were also studied, such as temperature, time and pulp density. The effect of pulp density was studied from 100 g/L to 700 g/L. Several experiments were conducted under the same condition to provide an average value of the PGM dissolution.

In the leaching experiment, the powder was poured into the glass beaker filled with a chloride solution at the working temperature. The solution was heated and agitated by a hot plate-magnetic stirrer for a certain leaching time. Filtration of the leaching solution was carried out after the samples were cooled down to room temperature. Fine porosity glass filter (G4 grade) with a pore size about $10-16 \,\mu\text{m}$ was utilized for the filtration. Several mL of $1 \,\text{kmol} \cdot \text{m}^{-3}$ HCl were added during the rinsing and filtration to keep the pH of the solution in the acidic region. The whole solution of each condition was then diluted for analysis. The element analysis was conducted by using ICP (SII, Seiko Instruments). The metal dissolution of PGM was calculated based on the percentage of dissolved PGM with the composition of PGM in the sample, as listed in Table 1.

4. Results and Discussion

At first, the PR sample of automotive catalyst residue was examined by using HCl and H_2O_2 leaching solution mixture without addition of water. H_2O_2 was added to increase the oxidation of PGM during leaching. The filtrated solutions become reddish. It suggests that $PdCl_4^{2-}$ and $PdCl_6^{2-}$ are formed in the leaching process.¹⁰ The color of chlorocomplex Pd is darker than that of Pt and Rh. Therefore, the filtrated leachate color is unable to be an indicator of PGM dissolution efficiency.

Figure 2 shows the effect of H_2O_2 addition into the raw solution of HCl on the dissolution of Pt, Pd and Rh. In the figure, the concentration of HCl exhibits the actual concentration in the leaching solution mixture. Addition of H_2O_2 in the raw solution of HCl, as much as up to 0.5 vol%, increases

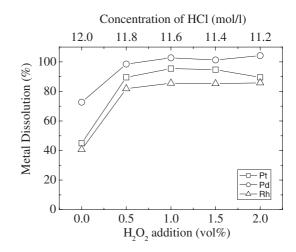


Fig. 2 Effect of H₂O₂ addition into the raw HCl leaching solution mixture.

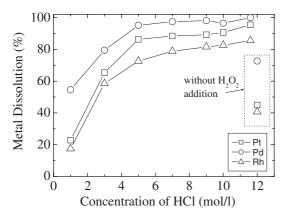


Fig. 3 PGM dissolution in the HCl solution with addition of 1 vol% H_2O_2 at $65^\circ C$ for 3 h.

the dissolution of PGM, dramatically. Addition of H_2O_2 by more than 0.5 vol% increases the PGM dissolution slightly. It was observed that H_2O_2 addition about 1 vol% gives optimum condition for the dissolution of PGM. However, H_2O_2 addition in higher amount to the leaching solution did not significantly increase PGM dissolution.

Based on the above result, $1 \text{ vol}\% \text{ H}_2\text{O}_2$ was added into the HCl leaching solution. In this case, the concentration of HCl was varied from 1 mol/L up to 10 mol/L by adding distilled water into the leaching solution. Figure 3 demonstrates that Pt, Pd and Rh dissolution increases with increasing the HCl concentration in the leaching solution with $1 \text{ vol}\% \text{ H}_2\text{O}_2$. At any HCl concentration, the order of PGM dissolution from the highest is Pd, Pt and Rh. The dissolution of Pt, Pd and Rh at 11.6 mol/L HCl was 95.5, 100 and 85.6%, respectively.

The results also show that the addition of H_2O_2 increases the PGM leaching in HCl solution. Bubble gas was formed and observed when H_2O_2 was added into the solution. It agrees well with reaction (2). This condition exhibits that chloro-complex formation of each PGM due to the addition of acid and chloric ion from HCl was occurred during the leaching, although the increase in PGM dissolution was not so high for the HCl concentration more than 5 mol/L. Possible routes of chloro-complexes formation are also suggested as shown in reaction (3) or (4). Here, H_2O_2 can take part in the leaching reaction. It can react with HCl to produce chloride components of high oxidation potential such as $Cl_2(aq)$ and HClO. These chloride species will be helpful to promote the leaching of PGM.

To elevate the dissolution of PGM by using lower HCl concentration, NaClO was selected to be a promoter in the leaching solution together with H₂O₂. The concentration of HCl was selected at 5 mol/L, that is the concentration where PGM dissolution was not higher than that of lower concentration of HCl addition (see Fig. 3). As shown in Fig. 4, the addition of NaClO (0–5 vol%) to the leaching solution gives the dissolution of Pt, Pd and Rh in the range of 86.1–88.8%, 95.8–98.7% and 72.0–76.9%, respectively. The addition of 3 vol% NaClO yields the dissolution of Pt, Pd and Rh of 87.7% (\pm 0.70%), 98.7% (\pm 0.83%) and 76.9% (\pm 1.29%), respectively.

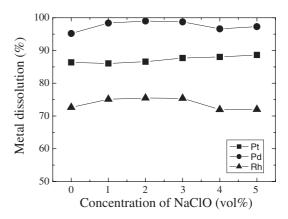


Fig. 4 PGM dissolution in NaClO system with $5\,kmol\cdot m^{-3}$ HCl and $1\,vol\%$ H_2O_2 at $65^\circ C$ for 3 h.

From the above results, the NaClO-HCl-H₂O₂ leaching solution system was proposed for further study. It composed of 3 vol% NaClO-5 mol/L HCl-1 vol% H2O2 which was added periodically during the leaching of PGM. The comparison between PGM dissolution from NaClO-HCl-H₂O₂ and HCl-H₂O₂ leaching solution system is shown in Fig. 5(a) for Pt, (b) for Pd and (c) for Rh. Both of the leaching solutions contained 1 vol% H₂O₂. In this figure, PGM dissolution from NaClO-HCl-H2O2 system is noted by dotted line, while HCl-H2O2 system is described by patterned bar, according to the concentration of HCl. In Fig. 5(a), the dissolution of Pt from NaClO-HCl- H_2O_2 system was still higher than 5 mol/L HCl-H₂O₂ system but lower than 7 mol/L HCl-1 vol% H₂O₂ [Fig. 5(b)]. However, Pd was almost completely dissolved in NaClO-HCl-H₂O₂ system with 5 kmol \cdot m⁻³ HCl. The dissolution in this system is close to that of 11.6 mol/L HCl-1 vol% H_2O_2 . In Fig. 5(c), the dissolution of Rh was in agreement with that of 8 mol/L HCl–1 vol% H_2O_2 solution. It was lower than $9\,mol/L$ HCl but still higher than 7 mol/L HCl-1 vol% H₂O₂.

In general, both of the leaching solutions lead to the dissolution of PGM with the order of Pd > Pt > Rh. It is quite different from the standard potential value which give the order of Rh > Pt > Pd. However, one can say that the solution system was rather complex to follow the standard potential alone to predict the leaching of PGM. In addition, kinetic factors also affect the PGM dissolution. More detail investigation of kinetic behavior of the leaching of PGM in the solution system is still underway. The results from the leaching by NaClO–HCl–H₂O₂ system also suggest that the presence of NaClO (up to 3 vol%) is effective to increase the dissolution of Pt, Pd and Rh about 3–5%. The previous study showed that metallic Pt was not dissolved in NaClO system.⁴ However, the increase of Rh dissolution with NaClO promoter agent was observed in this study.

Further evaluation to optimize leaching conditions of NaClO–HCl–H₂O₂ system was done by examining the effect of time, temperature and pulp density in the leaching of PGM. Figure 6 shows the effect of leaching time during the leaching for 6 h at 65° C. The reaction occurred quite fast. Prolonged the leaching time would not significantly affect the PGM dissolution. More than 1 h leaching time gave no

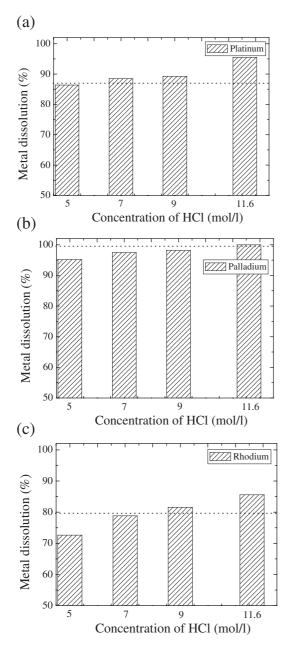


Fig. 5 Comparison of PGM dissolution between NaClO-HCl-H₂O₂ (3 vol%; 5 kmol·m⁻³; 1 vol%; dotted line) with HCl-H₂O₂ (5–11.6 kmol·m⁻³; 1 vol%; patterned bar) leaching solution. (a) Pt, (b) Pd and (c) Rh.

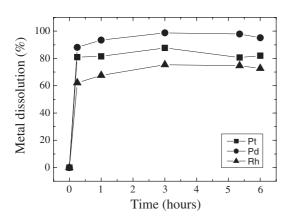


Fig. 6 Effect of leaching time up to 6 h to PGM dissolution for NaClO (3 vol%)–HCl (5 kmol $\cdot m^{-3})$ –H2O₂ (1 vol%) system.

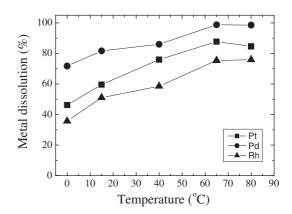


Fig. 7 Effect of temperature to the PGM dissolution during leaching for NaClO (3 vol%)–HCl (5 kmol·m⁻³)–H₂O₂ (1 vol%) system.

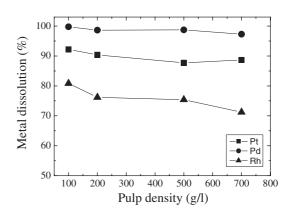


Fig. 8 Effect of pulp density to the PGM dissolution during leaching for NaClO (3 vol%)-HCl ($5 \text{ kmol} \cdot \text{m}^{-3}$)-H₂O₂ (1 vol%) system.

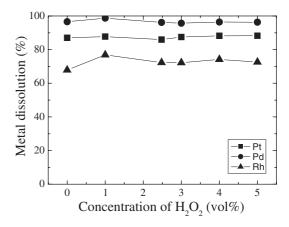


Fig. 9 Effect of H_2O_2 addition to the PGM dissolution in NaClO (3 vol%)– HCl (5 kmol·m⁻³) system.

significant effect to the PGM dissolution. In the experiment, finer powder was produced after leaching for longer period because of agitation. It makes the filtration process more difficult after leaching.

Figure 7 exhibits the effect of temperature on the leaching rates. Leaching at above 80°C might easily lead to vaporization of water and Cl-components from the relatively opened beaker glass. Therefore, it was not conducted in this examination due to some difficulties to control a constant

Conditions -		Leaching solution*		
		$NaClO + HCl + H_2O_2$	$HCl + H_2O_2$	NaClO + HCl
Pulp density	(g/L)	500	500	500
PR mass	(g)	1000	1000	1000
Solution volume	(L)	2	2	2
Reagents		Consumption/kg PR	Consumption/kg PR	Consumption/kg PR
NaClO	(mL)	60	_	60
Water	(mL)	1040	_	1107
HCl $(12 \text{ kmol} \cdot \text{m}^{-3})$	(mL)	833	1933	833
H ₂ O ₂ (30%)	(mL)	66.7	66.7	_
PGM products		Production g/kg PR	Production g/kg PR	Production g/kg PR
Pt	(g)	3.32	3.62	3.30
Pd	(g)	5.74	5.82	5.62
Rh	(g)	1.84	2.05	1.62
PGM extraction		Production (%)	Production (%)	Production (%)
Pt	(%)	87.7	95.5	87.1
Pd	(%)	98.7	100	96.6
Rh	(%)	76.9	85.6	67.9
Average of PGM dissolution	(%)	87.8	93.7	83.9

Table 2 Consumption and products of the leaching in the various chloride based leaching solutions.

*Detail composition of the leaching solutions is as follows:

• NaClO-HCl-H₂O₂ = 3 vol% NaClO-5 kmol·m⁻³ HCl-1 vol% H₂O₂

 $\bullet \, HCl\!-\!H_2O_2 = 11.6 \, kmol \!\cdot\! m^{-3} \; HCl\!-\!1 \, vol\% \; H_2O_2$

• NaClO-HCl = $3 \text{ vol}\% \text{ NaClO-5 kmol} \cdot \text{m}^{-3} \text{ HCl}$

pulp density and to keep the active chloride components in a relatively stable state under our present experiment conditions. In fact, it was found from the experiments that the PGM dissolution was not affected significantly by leaching temperature higher than 65°C.

Figure 8 shows the effect of pulp density on the PGM dissolution from 100 to 700 g/L. It was observed that the dissolution of Pt and Rh decreases in the higher pulp density. Only a slight decrease of Pd dissolution was observed during the leaching with pulp density higher than 100 g/L. The decrease of Rh dissolution is higher than Pt or Pd at pulp density higher than 100 g/L. It is understandable since the amount of powder became to be excessive in high pulp density. One can assume that in some extent higher pulp density would reduce the agitation efficiency. In addition, some PGM particles may not be reached by the leaching solution in the higher pulp density, since the particle size of PGM is in nanometer, which is located inside the support materials.¹²⁾ Particularly, the oxide support materials consume more HCl with increasing the pulp density and then lead to decreasing Cl ion concentration in the leaching solution, causing a low leaching rate of PGM.

Effect of H_2O_2 addition was also examined for the NaClO– HCl– H_2O_2 system. Figure 9 shows the effect of the amount of H_2O_2 addition to PGM dissolution. In general, addition of H_2O_2 more than 1 vol% does not increase the PGM dissolution. This result also confirms that NaClO might also take the role of oxidizing agent, as shown in reaction (7) and (8).

Table 2 summarizes the comparison of consumption and product of the leaching process among NaClO (3 vol%)–HCl

(5 kmol·m⁻³)–H₂O₂ (1 vol%), HCl (11.6 kmol·m⁻³)–H₂O₂ (1 vol%) and NaClO (3 vol%)–HCl (5 kmol·m⁻³). In the HCl–H₂O₂ system, the maximum concentration of HCl was selected to give the maximum PGM dissolution in the HCl based system. In the case of NaClO–HCl system, it demonstrates that NaClO can not completely replace H₂O₂ to be a sole oxidizing agent.

5. Conclusion

Various chloride based leaching solutions had been examined to dissolve PGM from automotive catalyst residue. The results are summarized below:

- Maximum dissolution of PGM in HCl-H₂O₂ system could be achieved by using HCl (11.6 mol/L)-H₂O₂ (1 vol%). The dissolution of PGM was 95.5, 100 and 85.6% for Pt, Pd and Rh, respectively, at 65°C for 3 h.
- The chloride in HCl can be substituted by NaClO. However, the substitution of Cl ions supplier from HCl to NaClO gives only limited capability to form chlorocomplexes of PGM. The optimum PGM dissolution by using NaClO (3 vol%)–HCl (5 mol/L)–H₂O₂ (1 vol%) was 87.7, 98.7 and 76.9%, for Pt, Pd and Rh, respectively. In addition, NaClO might also take a role as an oxidizing agent.

REFERENCES

- 1) H. Muraki and G. Zhang: Catalysis Today 63 (2000) 337-345.
- H. S. Gandhi, G. W. Graham and R. W. McCabe: J. Catal. 216 (2003) 433–442.

- 3) S. Matsumoto: Catalysis Today 90 (2004) 183-190.
- K. Liu, W. T. Yen, A. Shibayama and T. Fujita: Hydrometallurgy 2003—Proceeding of the 5th International Conference in Honor of Professor Ian Ritchie, vol. 2 (TMS, 2003) pp. 1617–1628.
- 5) M. H. H. Mahmoud: J. Mater. **3** (2003) 37–40.
- L. Bolinski and P. A. Distin: Proceeding of International Conference on Extractive Metallurgy of Gold and Base Metals, (AusIMM, 1992), pp. 277–280.
- K.-Y. A. Wu, K. D. Wisecarver, M. A. Abraham, N. Takach and N. Yang: *Proceeding of 17th International Precious Metals Conference*, (International Precious Metals Institute, 1993), pp. 343–349.
- 8) T. N. Angelidis: Topics in Catalysis 16-17 (2001) 419-423.
- A. J. Bard, R. Parsons and J. Jordan, eds.: Standard Potentials in Aqueous Solution, (Marcel Dekker, New York, 1985) pp. 339–365, 383–385.
- M. Pourbaix: Atlas of Electrochemical Equilibria in Aqueous Solutions, (NACE-Cebelcor, Houston, Texas, 1974) pp. 350–363, 378–383.
- 11) N. Takeno: Atlas of Eh-pH diagrams—Intercomparison of Thermodynamic Databases, (NIAIST, 2005) pp. 190–191, 198–199, 212–213.
- 12) G. W. Graham, A. E. O'Neill and A. E. Chen: Appl. Catal. A 252 (2003) 437–445.