Selective recovery of Fe(III), Pd(II), Pt(IV), Rh(III) and Ce(III) from simulated leach liquors of spent automobile catalyst by solvent extraction and cementation

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Abstract−A hydrometallurical process was developed to recover Fe(III), Pd(II), Pt(IV), Rh(III) and Ce(III) from the leach liquor of spent automobile catalysts. Fe(III) was first separated by extraction with tri-butyl-phosphate (TBP). Extraction of the raffinate with tri-isooctylamine (Alamine 308) led to co-extraction of Pd(II) and Pt(IV). They were separately stripped from the loaded Alamine 308 by using a mixture of HCl and thiourea with different concentration. After the recovery of HCl in the raffinate by extraction with tri-2-ethylhexyl amine (TEHA), Rh(III) was recovered by cementation with zinc metal powder. A process flow sheet with the corresponding McCabe-Thiele plots for extraction and stripping was proposed.

Keywords: Spent Automobile Catalyst, Palladium, Platinum, Rhodium, Solvent Extraction

INTRODUCTION

Platinum group metals (PGMs) are used in the automobile sector as catalysts, in fuel cells, in petroleum refining, as catalysts in a variety of organic reactions, in glass manufacturing sector and in jewelry. The combined catalytic properties of Pt, Pd and Rh are very important for automotive emission control [1]. Besides main PGMs components (Pt, Pd and Rh), the PGM catalysts contain other metals, such as Fe, Al, Ce, and La etc. [2-4]. After a certain period of active life, the catalysts become deactivated and are considered as spent catalysts. Since the demand for PGMs is increasing, recovery of PGMs together with other metals from the spent automobile catalysts has attracted much attention. In the recovery of PGMs from the spent catalyst, the PGMs are dissolved using high acid concentration in presence of an oxidizing agent [5,6]. The separation and recovery of PGMs from the leach liquor is very difficult because their physical and chemical properties are similar. Some methods, such as precipitation [2,7], ion exchange [8,9] and solvent extraction [1,10-17], are employed for the separation of PGMs.

Some works have been reported for the recovery of PGMs from the spent PGM catalysts employing solvent extraction, and a summary of the recovery of PGMs is shown in Table 1. TBP and 2-hydroxy-5-nonylacetophenone oxime (LIX 84I) offer selective extraction of Pd(II) from leach liquor at high acid concentration, while tri-caprylylmethylammonium chloride (Aliquat 336) can extract Pt(IV) [1,10-12,18]. The extraction and separation of Pt(IV), Pd(II), Ir(III) and Rh(III) is accomplished by adjusting the concentration of acid and Cyanex 923 (a mixture of four tri-alkyl phosphine oxides)/Cyanex 471 (tri-isobutylphosphine sulphide) [13,14]. However, the main disadvantage in these processes lies in the fact that non PGMs present in the raffinate after extraction of Rh(III) was not efficiently recovered. Since Fe(III) and Al(III) exist in most of the leach liquor of spent catalysts, precipitation of Fe(III) and Al(III) before extraction results in the loss of PGMs, in the consumption of reagent for neutralization of the leach liquor and in the low purity of final product. High acid concentration needed in stripping process is also a drawback in the commercialization of these methods.

In the present study, we developed a process for the recovery of PGMs from a leach liquor simulating those from the treatment of spent automobile catalyst containing Pd(II), Pt(IV), Rh(III), Fe(III) and Ce(III). Unlike the reported methods, all metals together with HCl in the leaching solution were recovered by using solvent extraction and cementation. For each extraction step, an optimum stripping condition which led to a pure solution was obtained. On the basis of the results, a process together with the optimum conditions was proposed to recover Pd(II), Pt(IV), Rh(III), Fe(III) and Ce(III) from the leaching solution of spent automobile catalysts.

EXPERIMENTAL

TBP (Sigma-Aldrich Co.), Alamine 308 (BASF Co.), TEHA (BASF Co.) were used without further purification. The concentration of the extractants used in the organic solution was varied from 0.1-2 M for TBP, 0.005-0.5 M for Alamine 308 and 0.1-2 M for TEHA. Kerosene (Samchun Pure Chem. Co.) and Decanol (Acros Organics Co.) were used as a diluent and modifier, respectively. Synthetic solution was prepared by dissolving appropriate amounts of PtCl$_4$ (99.9%), PdCl$_2$ (99.9%), RhCl$_3$·xH$_2$O (99.9%), CeCl$_3$ (99.5%) purchased from Alfa-Aesar Co., FeCl$_3$·6H$_2$O (97%) from Kanto Chemical Co. The composition of the synthetic solution was Fe(III)-

Table 1. A summary on recovery of PGMs from spent PGM catalysts by solvent extraction involving commercial extractant

Leach liquor, ppm	Extractant	Advantages	Disadvantages	Ref.
[HCl+HNO₃]-1.2 M, Pt-730, Al-20.000, In-660, Sn-300	Aliquat 336	Selective extraction of Pt with high purity was obtained	Simultaneous precipitation of Al, Sn and In from Pt free raffinate led to low purity of final products	[1]
3 M HCl, Pd-150, Pt-550, Mn-500, Ni-1000, Fe-1500, Cr-100	LIX 84I Alamine 336	Selective extraction of Pd by LIX 84I was obtained. Pt and Fe from Pd free raffinate were extracted by Alamine 336. Pt and Fe from the loaded organic were separated in stripping step	No information for recovery of the others such as Mn, Ni and Cr from the Pd, Pt and Fe free raffinate	[10]
1 M HCl, Pt-364, Rh-62, Al-13880, Mg-6980, Fe-1308	Aliquat 336	First Fe and Al were removal by precipitation and then selective extraction of Pt from the raffinate was obtained by Aliquat 336	Loss of Pt during precipitation of Fe and Al. The recovery of Fe, Al, Mg and Rh was carried out by precipitation resulting in low purity of final products	[11]
6 M HCl, Pt-123.1, Al-4583, Fe-254.2	TBP Aliquat 336 TEHA	TBP selectively extracted Fe and then selective extraction of Pt from Fe free raffinate was obtained by Aliquat 336. Finally all HCl was extracted by TEHA leaving Al in the raffinate		[12]
5 M H₂SO₄, Pt-101.3, Pd-52.9, Rh-50.1, Au-95.2, Al-135.2	Cyanex 923	Pd and Au were extracted by Cyanex 923 and then they were separated in stripping process. After heating to near dryness and leaching again, selective extraction of Pt was also obtained by Cyanex 923	High co-extraction of metals existed in each extraction process. High acid concentration was needed for stripping. Process including two leaching steps was very complicated	[13]
5 M H₂SO₄, Pt-102.7, Ir-103.1, Rh-51.8, Au-98.5, Al-53.7	Cyanex 471X	Ir, Ag and Au were extracted by Cyanex 471 and then they were separated in stripping process. After heating to near dryness and leaching again, selective extraction of Pt was also obtained by Cyanex 471	High co-extraction of metals existed in extraction process. High acid concentration was needed for stripping process. Process including two leaching step was very complicated	[14]
3 M HCl, Pd-150, Pt-550, Mn-500, Ni-1000, Fe-1500, Cr-100	TBP Aliquat 336	Pd was selectively extracted over the others by TBP. After removing Fe by precipitation from Pd free raffinate, selective extraction of Pt was obtained by Aliquat 336	Loss of Pt in Fe precipitation process. The recovery of Cr, Mn and Ni in raffinate is not mentioned	[18]

600 ppm, Pt(IV)-120 ppm, Pd(II)-50 ppm, Rh(III)-25 ppm, Ce(III)-5,000 ppm, HCl-6 M, which corresponded to that of the real leaching solution of spent automobile catalyst. The acidity of the solution was controlled by adding HCl (Daejung Co., 35%). The mixture of HCl and thiourea (Daejung Co., 96%) was used as a stripping reagent by varying the concentration of thiourea from 0.01 to 1 M in 0.5 M HCl solution. Zinc metal powder (Sigma-Aldrich Co., 99.99%) with different mass from 0.2 to 1.4 mg was used in the cementation process.

Extraction and stripping experiments were performed by mixing equal volumes (10 mL) of aqueous phase and organic solution for 30 min (extraction and stripping equilibrium was reached within 30 mins in initial tests) using a wrist action shaker (Burrel, model 75). After equilibrium, the two phases were separated with a separating funnel. Metal ion concentrations in the aqueous phase before and after extraction were determined by inductively coupled plasma-optical emission spectrometer (Spectro, Arcos). The distribution ratio, D, was calculated as the concentration of metal present in the organic solution to that part in the aqueous phase at equilibrium. The percentage of extraction and stripping is defined as:

$$\text{Extraction percentage} \tag{1}$$
$$= \frac{\text{equilibrium mass of metal in the organic}}{\text{initial mass of metal in the aqueous before extraction}} \times 100$$

$$\text{Stripping percentage} \tag{2}$$
$$= \frac{\text{equilibrium mass of metal in the aqueous after strippint}}{\text{initial mass of metal in the organic before stripping}} \times 100$$

The extraction/stripping isotherms were obtained by contacting aqueous phase and organic solution at a different A/O ratio phase from 1/5 to 5/1. McCabe-Thiele diagrams were constructed by plotting extraction/stripping isotherm together with operating line.

RESULTS AND DISCUSSION

1. Fe(III) Extraction

1-1. Extraction

In concentrated HCl solution, anionic species of Pd(II), Pt(IV), Rh(III) and Fe(III), such as $PdCl_4^{2-}$, $PtCl_6^{2-}$, $RhCl_6^{3-}$ and $FeCl_4^{-}$ are predominant [10,19,20]. Some works have reported that Fe(III) is selectively extracted over PGMs by solvating and amine extractants from concentrated HCl solution [12,20-22]. Therefore, in
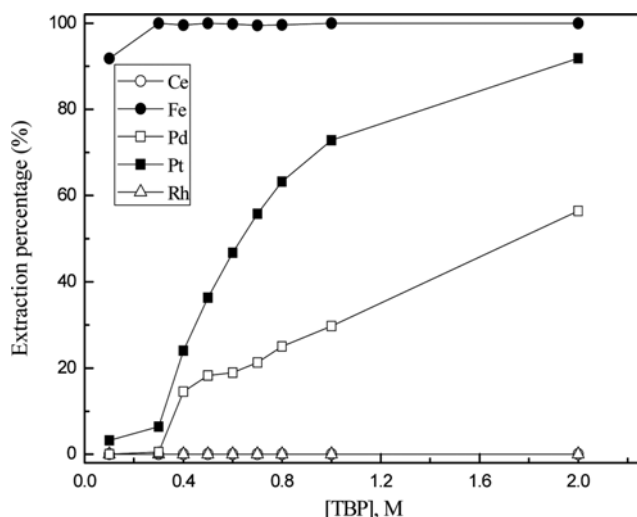
Fig. 1. Effect of TBP concentration on the extraction of Fe(III), Ce(III), Pt(IV), Pd(II) and Rh(III). Aqueous phase, ppm: Fe(III)-600, Ce(III)-5,000, Rh(III)-25, Pd(II)-50, Pt(IV)-120, [HCl]=6 M, [TBP]=0.1-2 M, Modifier-5% v/v decanol.
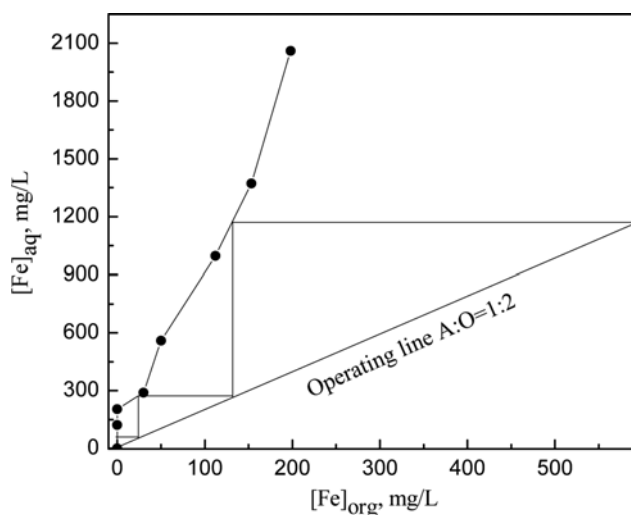

Fig. 2. Stripping isotherm of Fe(III) from 0.3 M TBP using water. Loaded 0.3 M TBP: Fe(III)-595.8 ppm, Pd(II)-0.25 ppm, and Pt(IV)-7.7 ppm. O/A=1/1-5/1.

order to selectively extract ferric ion from the leach liquor of the spent catalysts, TBP was used as an extractant. The extraction behavior of Fe(III), Pd(II), Pt(IV), Rh(III) and Ce(III) was investigated by varying TBP concentration from 0.1 to 2 M. In these experiments, 5% v/v decanol was added to the organic solution as a modifier. The organic solution was contacted to the synthetic solution containing Fe(III)-600 ppm, Pt(IV)-120 ppm, Pd(II)-50 ppm, Rh(III)-25 ppm, Ce(III)-5,000 ppm at 6 M HCl. The obtained results are shown in Fig. 1. Most of the Fe(III) was extracted at any TBP concentration, while the extraction percentage of Ce(III) and Rh(III) was negligible. The extraction percentage of Pd(II) and Pt(IV) increased steadily with the increase of TBP concentration.

Our data is in agreement with the reported data that ferric iron is selectively extracted over PGMs from concentrated HCl solution by solvating and amine extractants [12]. The extraction percentage of Fe(III) was the highest among the metal ions present in the solution at any TBP concentration. The charge density of PGMs is in the following order: $RhCl_6^{3-}>PdCl_4^{2-}>PtCl_6^{2-}$ [19]. The metal ion with higher charge density has a stronger tendency to be solvated by more water, resulting in less interaction with other counter ions. Therefore, the extraction percentage of Pt(IV) with the lowest charge density was the highest among Pt(IV), Pd(II) and Rh(III). The extraction efficiency of Pt(IV), Pd(II) and Rh(III) by TBP was in the order $RhCl_6^{3-}<PdCl_4^{2-}<PtCl_6^{2-}$. The negligible extraction of Rh(III) by TBP might be ascribed to the formation of $RhCl_5(H_2O)^{2-}$ which would not be extracted by TBP [23]. In hydrochloric acid solution, cationic species of Ce(III) such as Ce^{3+}, $CeCl^{2+}$ and $CeCl_2^+$ exist [24]. Therefore, Ce(III) was not extracted by TBP in this work. The extraction reaction of Fe(III), Pd(II) and Pt(IV) by TBP may be represented as follows [25]:

$$FeCl_{4,aq}^- + H_{aq}^+ + 3TBP_{org} = HFeCl_4(TBP)_{3,org} \qquad (3)$$

where the subscripts aq and org represent the aqueous phase and organic solution, respectively.

It can be concluded that selective extraction of Fe(III) over Pd(II), Pt(IV), Rh(III) and Ce(III) from 6 M HCl solution was obtained by adjusting TBP concentration. The optimum condition for the separation of Fe(III) from the leaching solution was found to be 0.3 M TBP.

1-2. Stripping

It has been reported that distilled water can strip Fe(III) from the loaded TBP [26]. Therefore, O/A ratio was varied from 1/5 to 5/1 to construct a McCabe-Thiele diagram for the stripping of Fe(III) from the loaded TBP by using distilled water. The loaded TBP was prepared by contacting the synthetic solution containing Fe(III)-600 ppm, Ce(III)-5,000 ppm, Pt(IV)-120, Pd(II)-50 ppm, Rh(III)-25 ppm at 6 M HCl with 0.3 M TBP in the presence of 5% v/v decanol at an O/A ratio of unity. The loaded TBP contained Fe(III)-595.8 ppm, Pd(II)-0.25 ppm, and Pt(IV)-7.7 ppm. McCabe-Thiele diagram (Fig. 2) shows that three-stage at an A/O ratio of 1/2 was enough to completely strip Fe(III) from the loaded 0.3 M TBP. According to the batch simulation experiments of three-stage counter-current stripping, Fe(III) was completely stripped from the loaded TBP and the concentration of the impurities in Fe stripping solution was negligible.

2. Pt(IV) and Pd(II) Extraction

2-1. Extraction

Fig. 1 indicates that it is difficult to separate Pt(IV) and Pd(II) by solvent extraction with TBP. Although di-octyl sulfide (DOS) has been known to selectively extract Pd(II) over Pt(IV) [27], the price of DOS is very high, which renders its commercial application to the separation of metals difficult. Since $PdCl_4^{2-}$ and $PtCl_6^{2-}$ are predominant in the HCl solution, amines are effective for extracting these species [20]. In this work, co-extraction of Pt(IV) and Pd(II) from the raffinate after removal of Fe(III) was tried by using tertiary amine. For this purpose, Alamine 308 was chosen and its concentration was varied from 0.005 to 0.5 M. In these experiments, 5% v/v decanol was added to Alamine 308 as a modifier. The composition of raffinate after extraction of Fe (III) was as fol-
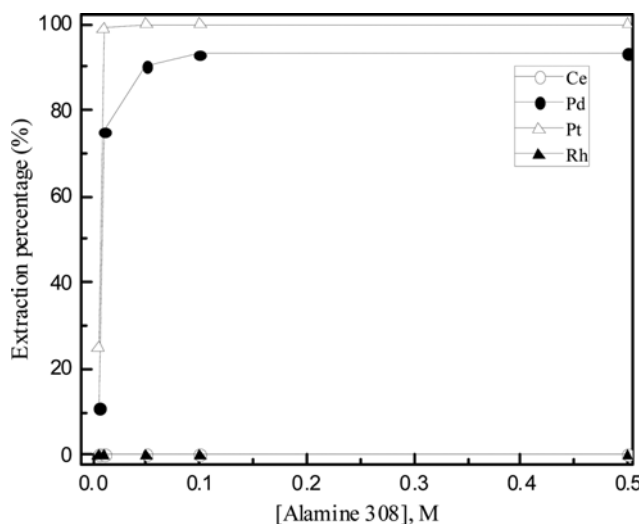
Fig. 3. Effect of Alamine 308 concentration on the extraction of Ce(III), Pt(IV), Pd(II) and Rh(III). Raffinate, ppm: Fe(III)-4.2; Ce(III)-5,000; Pt(IV)-112.3; Pd(II)-49.8 and Rh(III)-25, [HCl]=6 M, [Alamine 308]=0.005-0.5 M, Modifier-5% v/v decanol.

lows: HCl-6 M, Fe-4.2 ppm, Ce(III)-5,000 ppm; Pt(IV)-112.3 ppm; Pd(II)-49.8 ppm and Rh(III)-25 ppm. Fig. 3 shows that extraction percentage of Pt(IV) and Pd(II) increased with the increase of Alamine 308 concentration and reached a peak at 0.05 and 0.1 M Alamine 308, respectively and then was nearly constant with the further increase of extractant concentration. Since the charge density of $PtCl_6^{2-}$ is lower than that of $PdCl_4^{2-}$ [19], the extraction percentage of Pt(IV) was higher than that of Pd(II) at any Alamine 308 concentration. The co-extraction of Ce(III) and Rh(III) was negligible in these experimental conditions. The obtained results indicated that 0.1 M Alamine 308 was an optimum concentration for the selective extraction of both Pt(IV) and Pd(II) over Ce(III)
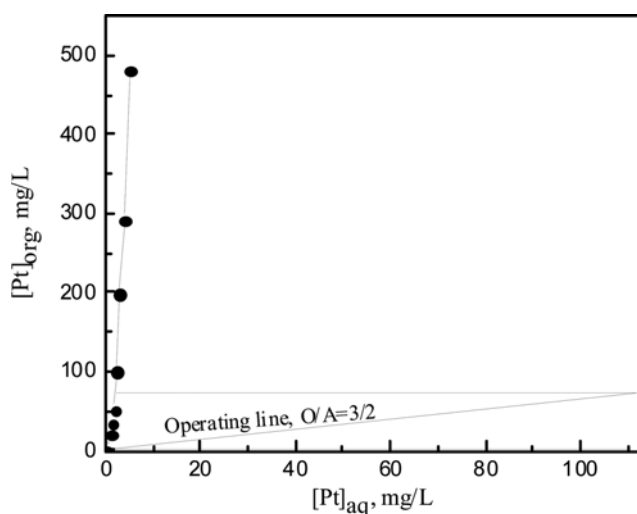

Fig. 4. Extraction isotherm of Pt(IV) by 0.1 M Alamine 308. Raffinate, ppm: Fe(III)-4.2; Ce(III)-5,000; Pt-112.3; Pd-49.8 and Rh-25; O/A=1/5-5/1, Modifier-5% v/v decanol.
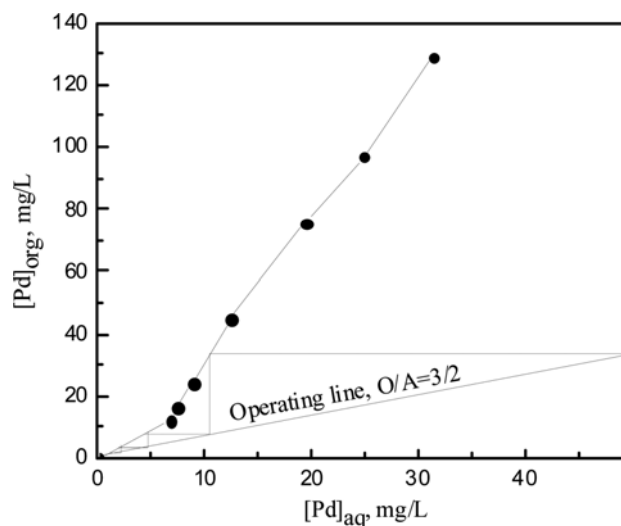

Fig. 5. Extraction isotherm of Pd(II) by 0.1 M Alamine 308. Raffinate, ppm: Fe(III)-4.2; Ce(III)-5,000; Pt(IV)-112.3; Pd(II)-49.8 and Rh(III)-25; O/A=1/5-5/1, Modifier-5% v/v decanol.

and Rh(III) from the raffinate because of extraction efficiency of two these metals and thus 0.1 M Alamine 308 was employed in further experiments.

To find the theoretical number of stages for complete extraction of Pt(IV) and Pd(II) from the raffinate containing Fe-4.2 ppm, Ce(III)-5,000 ppm, Pt(IV)-112.3 ppm, Pd(II)-49.8 ppm and Rh(III)-25 ppm, extraction isotherms for Pd(II) and Pt(IV) were obtained by contacting the raffinate with 0.1 M Alamine 308 at different O/A ratios from 1/5 to 5/1. McCabe-Thiele diagrams indicate that one theoretical extraction stage is needed to extract most of Pt(IV) at an O/A ratio of 3/2 (see Fig. 4), while four stages are needed for quantitative extraction of Pd(II) using 0.1 M Alamine 308 at an O/A ratio of 3/2 (see Fig. 5). The batch simulation experiments for four-stage counter-current extraction were performed with 0.1 M Alamine 308 at an O/A ratio of 3/2. From the batch simulation experiments, it was found that 99.9% of Pd(II) and Pt(IV) was extracted from the raffinate. The loaded organic solution containing 74.8 ppm Pt(IV), 33.2 ppm Pd(II) and 4.2 ppm Fe(III) was used for further stripping experiments.

2-2. Stripping

The interaction between Pt(IV)/Pd(II) and amines is very strong, and thus the mixture of thiourea and HCl is necessary to strip these metals from the loaded amines [10,11,20,28,29]. According to the previous works, it is possible to separate Pt(IV) and Pd(II) during the stripping by adjusting the concentration of thiourea in the mixture with HCl [10,11,20]. To selectively strip Pd(II) over Pt(IV), the loaded 0.1 M Alamine 308 was contacted with the mixture of 0.5 M HCl and 0.01 M thiourea by varying A/O ratio from 5/1 to 1/5. Table 2 shows that complete stripping of Pd(II) was obtained at any A/O ratio, while the stripping percentage of Pt(IV) was low at the same conditions. The stripping percentage of Pt(IV) increased from 4.6% to 32.7% with the increase of A/O ratio from 1/5 to 5/1. The obtained results indicate that Pt(IV) and Pd(II) can be separated from the loaded Alamine 308 by stripping with the mixture of HCl and thiourea. The optimum condition for the

Table 2. Stripping of Pd(II) from 0.1 M Alamine 308 using 0.5 M HCl+0.01 M thiourea

A/O ratio	Stripping percentage, %	
	Pt	Pd
1/5	4.6	97
1/3	9.3	100
1/2	13	100
1/1	19.5	100
2/1	26	100
3/1	26.6	100
5/1	32.7	100

The loaded organic solution containing 74.8 ppm Pt(IV), 33.2 ppm Pd(II) and 4.2 ppm Fe(III). All Fe(III) was stripped by 0.5 M HCl+ 0.01 M thiourea

selective stripping of Pd(II) over Pt(IV) from the loaded Alamine 308 was found to be an A/O ratio of 1/5.

The concentration of thiourea in the mixture should be increased to facilitate the stripping of Pt(IV) from the tertiary amines. Therefore, the concentration of thiourea in the mixture with 0.5 M HCl was increased to 1 M. After stripping of Pd(II) from the loaded 0.1 M Alamine 308, the stripped organic solution containing 67.8 ppm Pt(IV) was further contacted to this mixture by varying the A/O ratio from 5/1 to 1/5. The McCabe-Thiele plot for the stripping of Pt(IV) from the loaded Alamine 308 indicates that two theoretical stripping stages are needed to strip Pt(IV) at an O/A ratio of 2/1 (see Fig. 6). According to the batch simulation experiments of two-stage counter-current stripping, Pt(IV) was completely stripped from the loaded Alamine 308.

3. Rh(III) Cementation

Figs. 1 and 3 indicate that the separation of Rh(III) and Ce(III) from 6 M HCl by solvent extraction was difficult. To separate these metals from the raffinate after extraction of Fe(III), Pt(IV) and
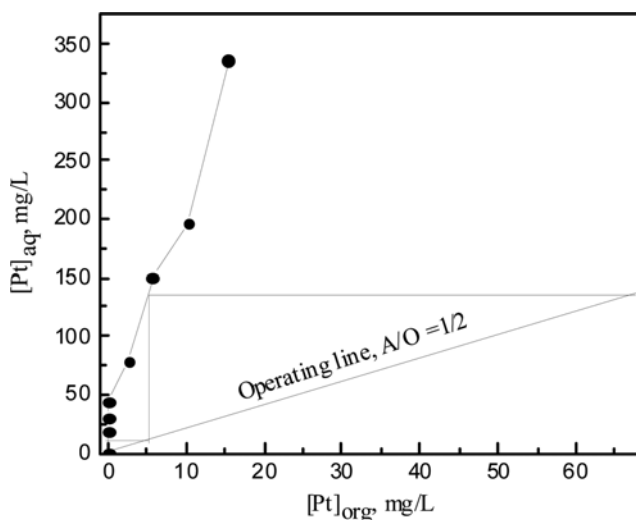

Fig. 6. Stripping isotherm of Pt(IV) from 0.1 M Alamine 308 using 0.5 M HCl+1 M thiourea. Loaded 0.1 M Alamine 308: Pt(IV)-67.8 ppm. O/A=1/1-5/1.
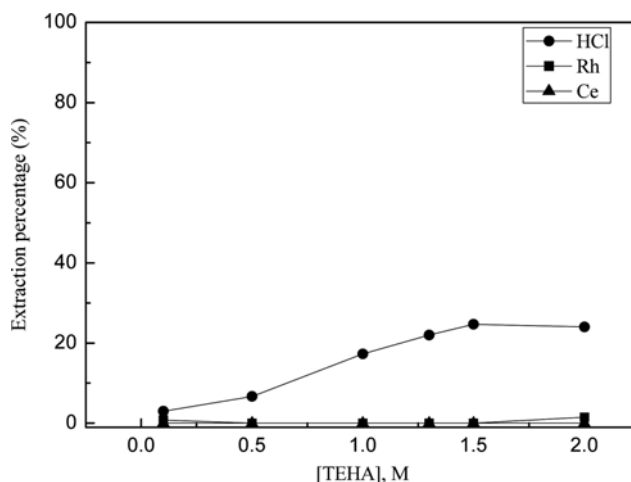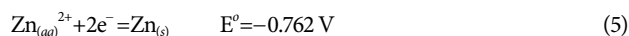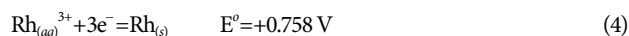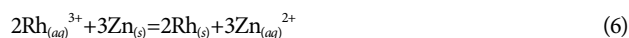
Fig. 7. Effect of TEHA concentration on the extraction of HCl, Ce(III), and Rh(III). Raffinate, ppm: Ce(III)-5,000, Rh(III)-25, [HCl]=6 M, [TEHA]=0.1-2 M.

Pd(II), we studied the cementation of Rh(III). Because the concentration of HCl in the raffinate was very high (6 M), decrease of HCl concentration should be done before cementation. Some reported studies indicate that TEHA could extract HCl [12,30]. Therefore, TEHA was used for the extraction of HCl from the raffinate containing 5,000 ppm-Ce(III) and 25 ppm-Rh(III) at 6 M HCl. Fig. 7 shows the variation in extraction percentage of Ce(III), Rh(III) and HCl with the TEHA concentration from 0.1 to 2 M. The extraction percentage of Rh(III) and Ce(III) was negligible at any TEHA concentration, while the extraction percentage of HCl increased from 5 to 29% with the increase of TEHA concentration. Based on an optimum condition reported in the literature [12], batch simulation experiments of five-stage counter-current extraction of HCl from the raffinate using 1 M TEHA was carried out at an O/A ratio of 5/1. Quantitative extraction of HCl was obtained by this condition and the composition of the raffinate was 5,000 ppm Ce(III) and 22.4 ppm Rh(III), and 0.5 M HCl, which was employed in further experiments.

Since Rh(III) was not extracted by TBP and Alamine 308 in these experiments, the Rh(III) in the raffinate after HCl extraction was recovered by cementation with zinc metal. The standard reduction potentials of Rh(III) and Zn(II) are given as follows [31]:

$$Rh_{(aq)}^{3+}+3e^- =Rh_{(s)} \qquad E^o=+0.758 \text{ V} \tag{4}$$

$$Zn_{(aq)}^{2+}+2e^- =Zn_{(s)} \qquad E^o=-0.762 \text{ V} \tag{5}$$

The overall reaction is expressed in Eq. (6) [31]:

$$2Rh_{(aq)}^{3+}+3Zn_{(s)}=2Rh_{(s)}+3Zn_{(aq)}^{2+} \tag{6}$$

where the subscripts aq and s represent the aqueous phase and solid, respectively.

The concentration of Rh(III) in the raffinate after HCl extraction was 22.4 ppm. The stoichiometry of Eq. (6) indicates that the zinc concentration in the Rh(III) solution should be higher than 20 ppm to cement Rh(III). Therefore, 20 mL of the raffinate containing 5,000 ppm Ce(III) and 22.4 ppm Rh(III) at 0.5 M HCl was
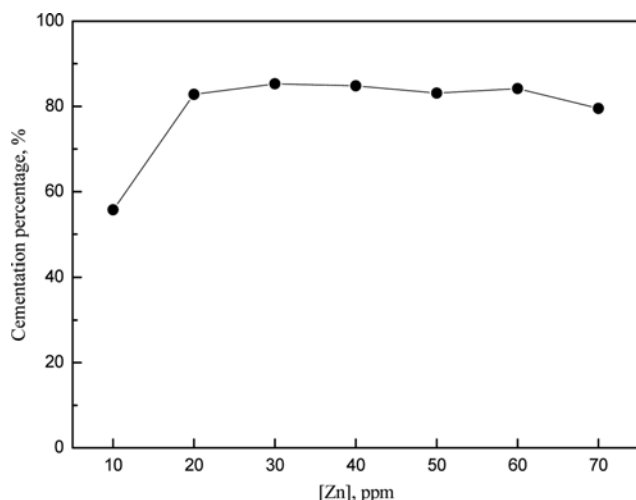
Fig. 8. Cementation of Rh(III) by Zn metal powder. Raffinate, ppm: Ce(III)-5,000, Rh(III)-22.4, [HCl]=0.5 M; [Zn]=10-70 ppm.

treated by varying the mass of zinc metal power from 0.2 to 1.4 mg. Fig. 8 shows the variation in cementation percentage of Rh(III) as a function of the concentration of zinc in the solution. The cementation percentage of Rh(III) increased from 56% to 83% with the increase of the concentration of zinc from 10 to 20 ppm and was constant with the further increase of zinc concentration. Therefore, 20 ppm of zinc was chosen as an optimum condition for the separation of Rh(III) from Ce(III). After the cementation of Rh(III) with zinc metal, the filtrate contained 3.8 ppm Rh(III) and 17.8 ppm Zn(II) and the purity of the Ce(III) in the filtrate was 99.6%.

The overall process for the separation of Fe(III), Pd(II), Pt(IV), Rh(III) and Ce(III) from a simulated leach liquor of a spent auto-

mobile catalyst by solvent extraction and cementation is presented in Fig. 9. Compared to the processes when iron was removed by precipitation [11,18], selective extraction of Fe(III) over Pt(IV), Pd(II), Ce(III) and Rh(III) by solvent extraction led to the decrease in the loss of PGMs from the leach liquor. Both Pt(IV) and Pd(II) from Fe(III) free raffinate was extracted in one extraction step and their complete separation was accomplished during the stripping process. HCl was recovered by extraction with TEHA, which led to the decrease in the consumption of neutralizing reagent to get the final metal product. Cementation of Rh(III) by zinc power results in a pure Ce(III) solution.

CONCLUSION

The separation and recovery of Fe(III), Pd(II), Pt(IV), Rh(III) and Ce(III) from a simulated leach liquor of a spent automobile catalyst was investigated by solvent extraction and cementation. Complete separation of Fe(III) from the leach liquor containing Pt(IV), Pd(II), Ce(III), and Rh(III) at 6 M HCl was obtained by extraction with TBP. The Fe(III) from the loaded TBP was completely stripped by water. The use of Alamine 308 led to selective extraction of Pt(IV) as well as Pd(II) from the Fe(III) free raffinate. Extraction isotherm indicated that quantitative extraction of both Pt(IV) and Pd(II) was achieved after four-stage counter-current extraction at an O/A ratio of 3/2. Pd(II) was selectively stripped from the loaded Alamine 308 by using the mixture of HCl and thiourea, and then complete stripping of Pt(IV) was obtained in two stages by increasing the concentration of thiourea in the mixture with HCl. From the Pt(IV) and Pd(II) free raffinate, most of HCl was recovered by five counter-current stage extraction with TEHA. The Rh(III) after the recovery of HCl was recovered by cementation with zinc metal powder. Based on the obtained results, a process flow sheet of the process for the recovery of Fe(III), Pd(II), Pt(IV), Rh(III) and Ce(III) from leach liquor of spent automobile catalysts was developed.

Fig. 9. Conceptual flowsheet for the separation and recovery of PGMs from a simulated leach liquor of a spent automobile catalyst (Tu: thiourea).

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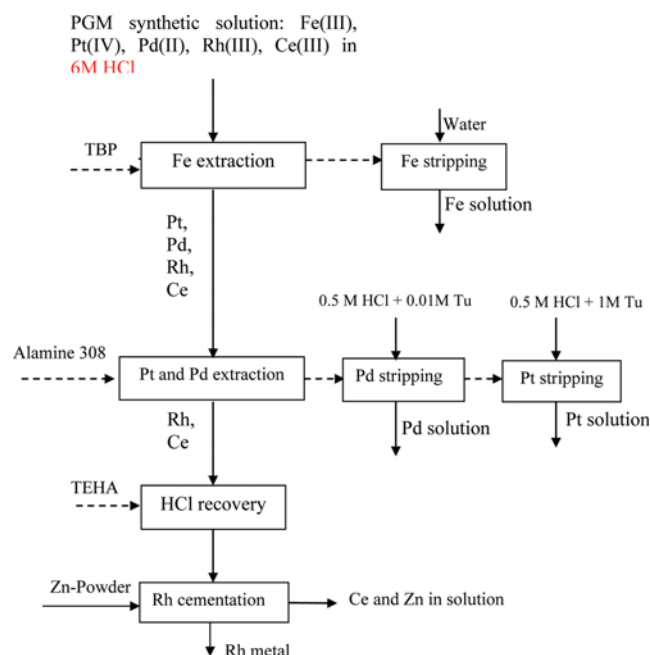
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