

Platinum Recovery Using Calcium Vapor Treatment*¹

Toru H. Okabe¹, Yoshihiro Kayanuma^{1,*2}, Sachiko Yamamoto^{2,*3} and Masafumi Maeda¹

¹Institute of Industrial Science, The University of Tokyo, Tokyo 153-8505, Japan

²Department of Metallurgical Engineering, Chiba Institute of Technology, Narashino 275-0016, Japan

To develop an effective process for the recovery of precious metals from scrap, a new platinum (Pt) extraction process using alloy formation by calcium (Ca) vapor and successive leaching with an aqueous solution were investigated. Pure Pt samples were reacted with Ca vapor at constant temperatures ranging between 1073 and 1173 K for three to twelve hours, and Ca–Pt alloy samples were synthesized. The obtained Ca–Pt alloy was then dissolved in aqua regia or in an aqueous HCl solution at room temperature. Platinum was recovered from the leaching solution by conventional $(\text{NH}_4)_2\text{PtCl}_6$ precipitation method, and the amount of Pt obtained by each process was analyzed. It was found that more than 90% of the Pt was recovered by this process. After Ca vapor treatment, 100% of the Pt was dissolved when kept in aqua regia for one hour, whereas only 14% of untreated pure platinum was dissolved when kept in aqua regia for four hours. In some experiments, the obtained Ca–Pt alloy samples were oxidized in air for reducing the amount of acid needed for dissolution. Although Pt hardly dissolves in aqueous HCl solution at room temperature, it was found that Ca vapor treatment followed by oxidation is effective in increasing the rate of dissolution in aqueous HCl solution.

(Received April 2, 2003; Accepted May 12, 2003)

Keywords: platinum, scrap recycling, calcium, leaching, calcium–platinum alloy, extraction, precious metals

1. Introduction

Platinum group metals (PGMs) are widely used in several applications such as auto-catalysts, because these elements are corrosion and heat resistant, and have various catalytic properties. Auto-catalysts containing PGMs that are used in the automobile industry have become essential in order to comply with environmental regulations, and the demand for PGMs is therefore increasing.¹⁾ Although PGMs are important elements for the industry, they are rare, and large amounts of energy and other resources are required to extract them from mineral resources. Furthermore, a large amount of waste is generated during the processes of extracting and refining PGMs.

In order to preserve these limited resources, it is extremely important to recover PGMs from scrap. In reality, however, this is not easy because most of the scrap containing PGMs has a complicated structure, and contains very small amounts of PGMs compared to other body materials. For example, PGMs in auto-catalyst scrap exist in a ceramic substrate, which has a honeycomb structure with a large surface area.¹⁾

As PGMs are chemically stable and do not react with most acids, it is difficult to extract them from scrap. Therefore, the whole body of scrap is smelted or dissolved in a large amount of strong acid to extract the PGMs.²⁾ In the current acid leaching process, it takes several hours to dissolve the scrap and a large amount of waste solution containing heavy metals and strong acid is generated. Therefore, it is important to develop an effective leaching process to recover PGMs from scrap. In the past, precious metals are collected in molten metal.^{2–7)} This classical metal-collection method using liquid metal as a collector metal (*e.g.* Cu, Sn, Pb) is effective and satisfactory for recovering precious metals but not suitable

for extracting platinum directly from solid scrap.

Taking into account the background mentioned above, the authors initiated a systematic study on a new platinum extraction process.^{8,9)} The concept of the investigated process is schematically illustrated in Fig. 1. One can see from the figure that calcium vapor supplied in its vapor form was used as an extraction medium at elevated temperature. Figure 2 shows the process chart of platinum recovery investigated in this study as well as the conventional process. The process employed in this study involves alloy formation using calcium vapor, and successive leaching with an aqueous solution. This process is based on the fact that PGMs have a strong affinity with alkaline earth elements¹⁰⁾

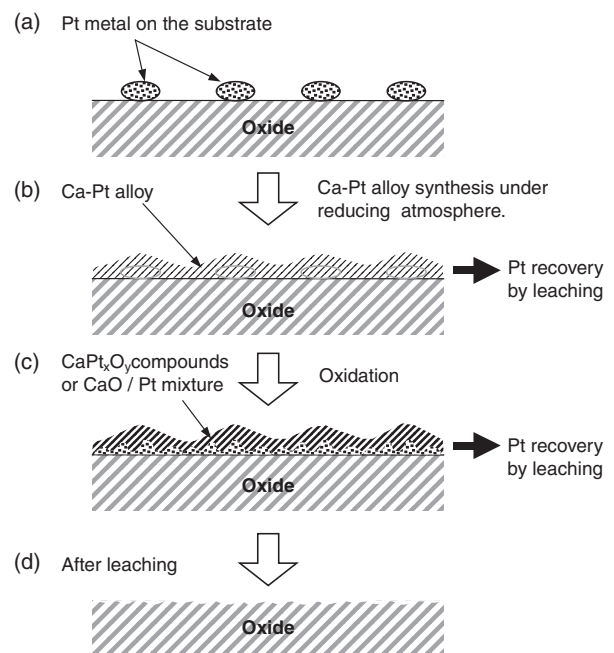


Fig. 1 Platinum recovery process by using calcium metal as an extraction medium.

*¹A Part of This Study was Presented at the Autumn Meeting of the Japan Institute of Metals, held in Osaka, on 3 November 2003.

*²Graduate Student, The University of Tokyo.

*³Undergraduate Student, Chiba Institute of Technology. Present address: Fujitsu LSI Solution Ltd., Kawasaki 212-0013, Japan.

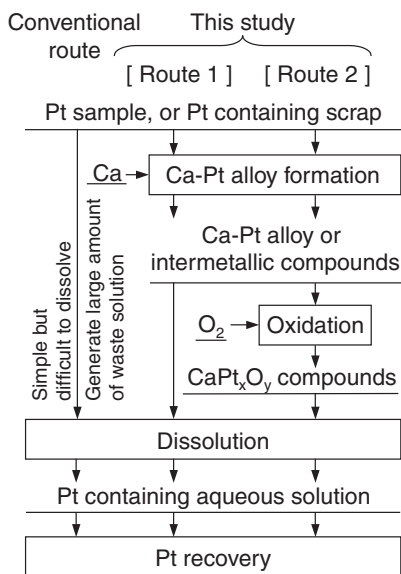


Fig. 2 Various routes of platinum recovery process.

and when they are alloyed with these reactive metals, PGMs in these compounds dissolve at ambient temperatures much more easily than they do in their pure form. Several compounds, such as Ca_5Pt_2 , Ca_5Pt_3 , are known¹¹⁾ to exist in the Ca–Pt system as shown in Fig. 3, and these compounds are expected to dissolve in acid. In Fig. 3, vapor pressure of calcium in the liquid alloy region of the Ca–Pt system is plotted for reference. One can see from the figure that the vapor pressure of calcium ranges between 10^{-3} and 10^{-2} atm at the experimental temperature (1173 K), and it can easily be supplied to scrap with complicated structures in its vapor form. The vapor pressure of platinum is more than trillion (ten to the fifteenth power) times smaller than that of calcium metal,¹²⁾ and it remains in the scrap during the process even at elevated temperatures. Keeping these properties in mind, a platinum recovery process using calcium vapor as an extraction medium was designed, and its effectiveness was investigated through fundamental experiments.

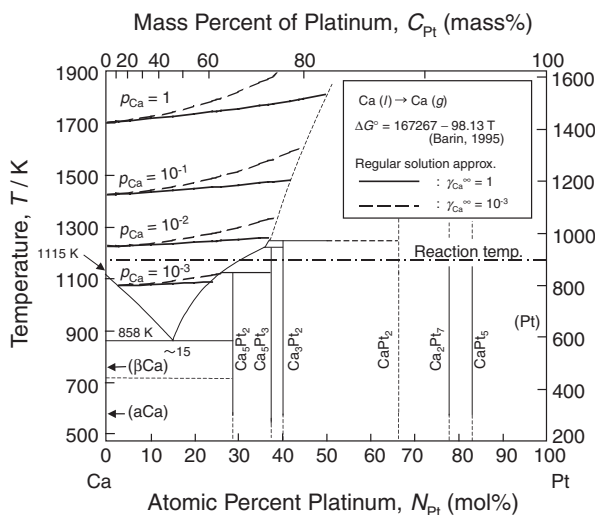


Fig. 3 Phase diagram of Ca–Pt binary system,¹¹⁾ and calculated vapor pressure of calcium in the Ca–Pt liquid alloy.

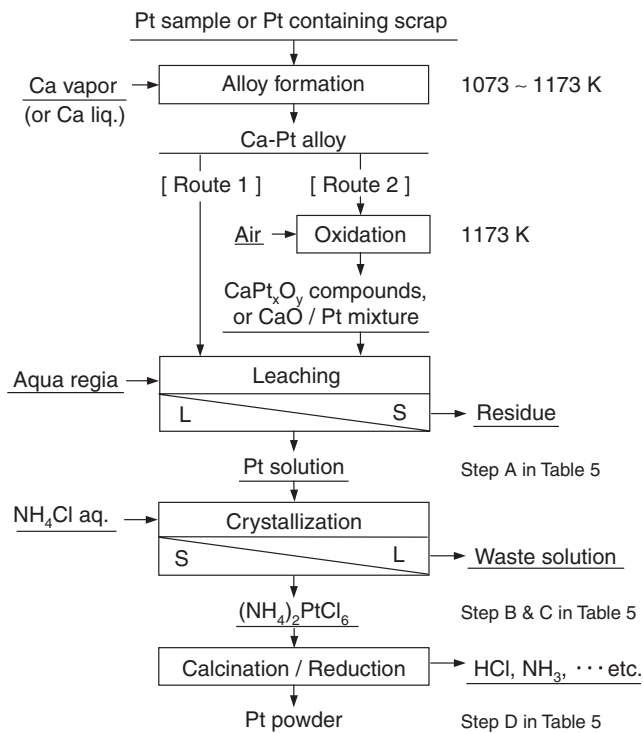


Fig. 4 Platinum recovery process using calcium as an extraction medium.

2. Experiment

Figure 4 shows the detailed material flowchart for the platinum recovery process using calcium as an extraction medium that was investigated in this study. The experiment consists of three major steps: alloy formation, leaching with acid, and platinum recovery from an aqueous solution. In some experiments, the obtained Ca–Pt alloys were oxidized in air (see Route 2 in Fig. 4) to decrease the amount of acid necessary for dissolution.

A schematic diagram of the experimental apparatus used for alloy formation is shown in Fig. 5, and the purity and form of the starting materials used in this study are listed in Table 1. About 0.5 to 1.1 g of platinum powder (0.2 μm) or a platinum plate (0.2–0.4 mm thick) was placed on each stainless steel sample holder supported by a stainless steel container. About

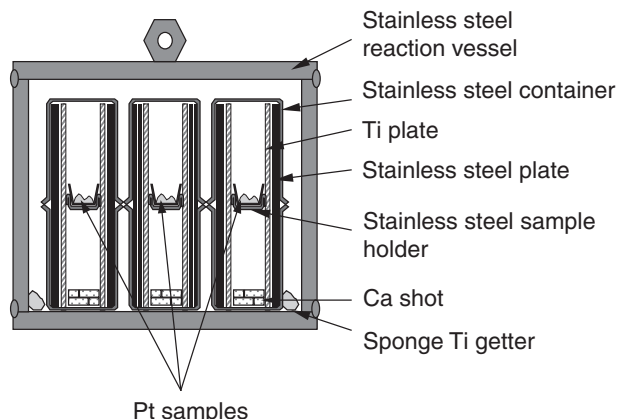


Fig. 5 Schematic diagram of experimental apparatus for calcium deposition on platinum.

Table 1 Starting materials used in this study.

Materials	Form	Purity or conc. (%)	Note
Pt (a)	Powder	99.9 up	0.2 μm dia.
Pt (b)	Plate	99.5 up	0.4 mm t
Pt (c)	Plate	99.9 up	0.2 mm t
Ca	Chip	99.0 up	10–20 mm
CaCO ₃	Powder	99.5 up	
NH ₄ Cl	Powder	99.0 up	
Ti	Sponge		1.0–2.0 g
HCl	Aqueous	35.0*	
HNO ₃	Aqueous	60.0*	
H ₂ O ₂	Aqueous	31.0*	

*: Concentration of the solution.

2 g of calcium lumps were placed at the bottom of the container. The calcium was physically isolated from the platinum sample, and its vapor was supplied to the platinum sample at unit activity via the gas phase while heating. As shown in Fig. 5, three to seven sets of stainless steel containers containing platinum and calcium samples were installed in a thick-walled stainless steel reaction vessel and were sealed by tungsten inert gas (TIG) welding. A sponge titanium was also placed at the bottom of the vessel for gettering nitrogen gas in the system.

The sealed reaction vessel was then heated in an electric furnace maintained at a constant temperature ranging between 873 and 1173 K, and pure platinum samples were reacted with calcium vapor. Some representative experimental conditions of alloy formation are summarized and listed in Table 2. After three hours of reaction at constant temperature, the reaction vessel was taken out of the furnace, and quenched in water. The samples in the container were mechanically recovered at room temperature, and subjected to the following oxidation or leaching process.

In some experiments, some of the obtained Ca–Pt alloy was oxidized in air before leaching in order to reduce the amount of acid necessary for dissolution. With this procedure, hydrogen gas generation by oxidative dissolution of the Ca–Pt alloy during leaching is suppressed. The oxidation of

the alloy was carried out at 1173 K for 24 hours in air using samples weighing about 0.4 to 1 g. The mass gain of the samples after oxidation was measured, and the phases before and after oxidation were analyzed.

The obtained Ca–Pt alloys or the oxidized samples were dissolved in aqua regia (nitrohydrochloric acid, a 3 : 1 mixture of concentrated HCl and HNO₃ aqueous solutions) or in an aqueous HCl solution at room temperature. For each 0.5 g of sample, 40 ml of aqua regia or concentrated aqueous HCl solution was used for dissolution. After dissolving the samples, the solid residue in the leaching solution was filtered using filter paper (0.03 μm pore size, ADVANTEC, 5C, ϕ 55 mm), and the obtained solution was subjected to a series of procedures for platinum recovery.

Platinum dissolved in the solution was extracted by precipitating diammonium hexachloroplatinate (IV), (NH₄)₂PtCl₆. This is the conventional procedure for platinum recovery.¹³⁾ In order to achieve effective precipitation of platinum salt, nitric acid and excess hydrochloric acid in the solution was removed before the precipitation procedures. For oxidizing Pt (II) to Pt (IV), 1 ml of aqueous H₂O₂ was added to the solution, and the solution was dried once by heating. Precipitation was carried out by adding 10 ml of 1 N HCl aq. and 40 ml of saturated NH₄Cl solution to the solution at room temperature. After the precipitation procedure, the obtained (NH₄)₂PtCl₆ precipitate was aged at 343–353 K (70–80°C) for about an hour by adding 20 ml of saturated NH₄Cl solution into the solution/precipitate mixture.

The solid yellow (NH₄)₂PtCl₆ precipitate powder containing NH₄Cl was recovered by filtration, and dried at 413 K (140°C). The dried powder was weighed, and then transferred to an alumina crucible and heated in air using a gas burner. By heating the precipitate, the ammonium and hydrochloric species in the sample were removed to the gas phase. After this thermal decomposition procedure, pure platinum powder was obtained in the crucible.

From the mass of obtained platinum in the sample, the yield in each process was analyzed. A chemical analysis of the solution was carried out using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The solid

Table 2 Experimental conditions of Ca–Pt alloy formation, and analytical results of the obtained alloy.

Sample #	Mass of Pt	Supplied form of Ca	Mass of Ca	Reaction temp.	Reaction time	Analytical results after reaction		
						Mass of obtained alloy	Composition of alloy ⁺ (mass %)	
							$w_{\text{alloy}}/\text{g}$	Ca, C_{Ca}
	w_{Pt}/g		w_{Ca}/g	T/K	t_{R}/h			
A	1.00	Vapor	2.09	1073	3	1.09	26.8	73.2
B	0.51	Vapor	2.10	1073	3	0.56	13.2	86.8
C	0.51	Vapor	2.10	1173	3	0.68	56.8	43.2
D	1.01	Vapor	2.07	1173	3	1.15	21.4	78.6
E	0.51	Vapor	2.09	1173	3	0.62	22.4	77.7
F	5.97	Liquid	6.10	1173	12	7.17	43.6	56.4
							52.6*	47.4*
G	5.59	Liquid	3.80	1173	12	8.84	38.7	61.3
							42.2*	57.8*

⁺ Determined by EDS.

* Determined by ICP.

samples were observed using scanning electron microscopy (SEM) after drying, and the composition of the sample was determined by both an energy dispersive X-ray spectrometer (EDS) and an ICP-AES. Phases in the sample were identified using an X-ray diffraction analysis (XRD).

3. Results and Discussion

The Ca–Pt alloy was not obtained when the reaction temperature was lower than 973 K. It was found that the vapor pressure of calcium at this temperature ($p_{\text{Ca}} = 1.2 \times 10^{-4}$ atm at 973 K) was too low for alloy formation. Table 2 contains some representative results of the Ca–Pt alloy formation. When the platinum sample was exposed to Ca vapor at temperatures above 1073 K ($p_{\text{Ca}} = 9.4 \times 10^{-4}$ atm at 1073 K), the Ca–Pt alloy containing more than 13% calcium by mass was successfully formed. In some experiments, a Ca–Pt alloy containing more than 50% calcium by mass was obtained after reaction at 1173 K (e.g. Exp. # C in Table 2). It was difficult to collect the alloy powder from the reaction vessel without any loss when opening the vessel by a lathe turning machine. In order to verify the reproducibility of platinum recovery from the alloy, a large amount of Ca–Pt alloy was synthesized by reacting platinum and calcium in a tantalum crucible at 1173 K (Exp. # F & G in Table 2). These alloy samples as well as the alloys synthesized by a vapor phase reaction were used in the dissolution experiment.

Figure 6 shows an SEM image of the Ca–Pt alloy obtained by reacting platinum powder and calcium vapor at 1173 K for 3 hours (cf. Exp. # E in Table 2). Figures 6(b) and (c) are the corresponding EDS images of the calcium and platinum. One can see from the figures that the surface of the alloy is homogeneous within the sensitivity of the EDS. The XRD analysis identified the phases present in the alloys to be pure calcium and platinum, but it was difficult to identify the intermediate phases in the Ca–Pt system.

Results of the oxidation of the Ca–Pt alloy at 1173 K for 24 hours in air are summarized and listed in Table 3. About 20% gain in mass was observed after oxidation of the alloy. The fifth column of Table 3 lists the mass of the obtained samples after oxidation. In the same column, the calculated mass was also listed for reference. This calculated mass was determined based on the mass and composition of the starting alloy, assuming the reaction $\text{Ca–Pt alloy} + \text{O}_2 \rightarrow \text{CaO} + \text{Pt}$. Considering the errors made in weighing the alloy powders, the calculated values are in agreement with the measured values. Figure 7 shows an SEM image of the sample after oxidation of Ca–Pt alloy, and the XRD pattern of the sample. After oxidation of the Ca–Pt alloy, the ternary oxide phase of Ca_4PtO_6 was identified with platinum and CaO. These results show that the Ca–Pt alloy was converted to a Pt/CaO/ Ca_4PtO_6 mixture after oxidation.

Table 4 shows the results of the experiments on the dissolution of the Ca–Pt alloys and the oxidized samples. The dissolution results for pure platinum (Exps. # 1 & 6) and for samples obtained after oxidation (Exps. # 4, 5, 9, 10) are also listed for comparison. Experiments # 1–5 in Table 4 show the results of dissolution in aqua regia, and Experiments # 6–10 show the same for an aqueous HCl solution. Almost 100% of the platinum was dissolved after leaching with aqua regia in

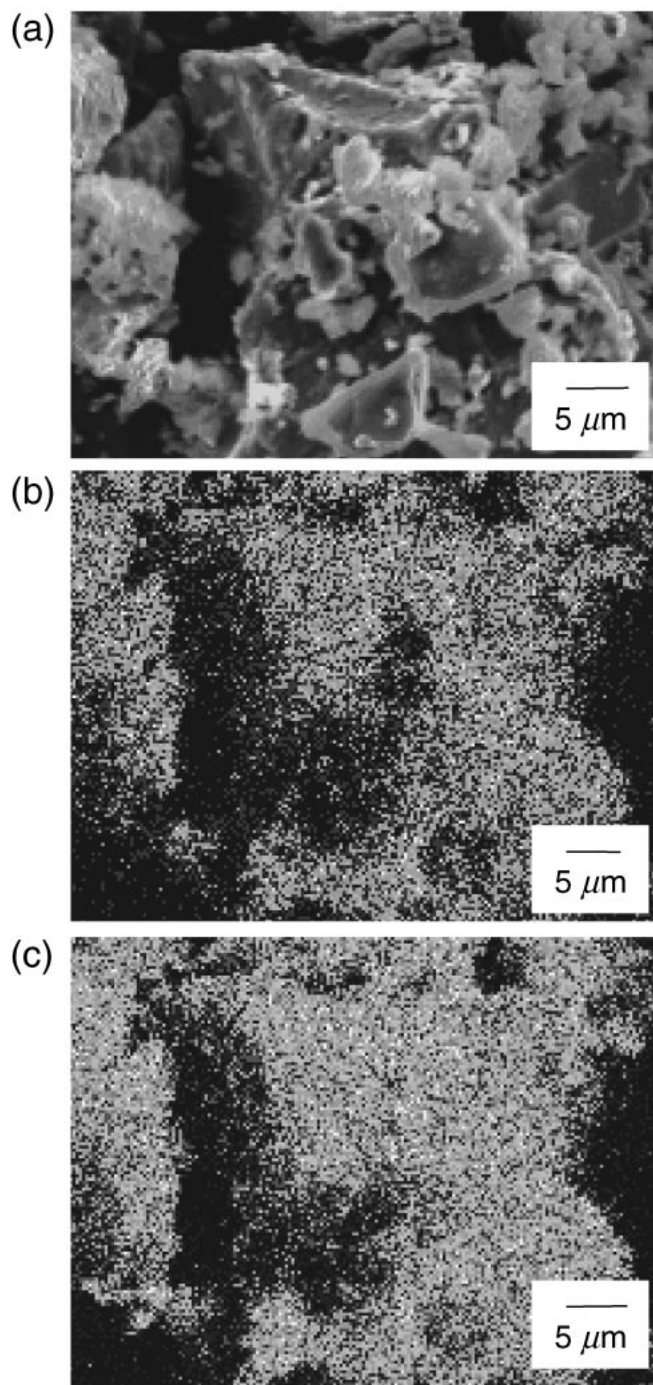


Fig. 6 (a) SEM image of Ca–Pt alloy, and corresponding EDS images of (b) Ca and (c) Pt.

Exps. # 2, 3, 4, and 5. When samples were dissolved after oxidation (Exps. # 4, 5, 9, and 10), hydrogen evolution during leaching was suppressed because the metallic calcium was already oxidized. As shown in Exps. # 4 & 5 in Table 4, 100% of the oxidized samples were dissolved in aqua regia. These results show that it is possible to reduce the amount of acid necessary for the dissolution of platinum by using a calcium treatment followed by oxidation. Interestingly, it was found that hardly any platinum in the alloy was dissolved by leaching the Ca–Pt alloy with an aqueous HCl solution (Exp. # 7 & 8). Although pure platinum hardly dissolves in an aqueous HCl solution at room temperature, calcium vapor

Table 3 Results of Ca–Pt alloy oxidation experiment, and analytical results of the obtained compounds.

Sample #	Mass of feed alloy* ¹ $w_{\text{alloy}}/\text{g}$	Reaction temp. T/K	Reaction time t_{ox}/h	Mass of obtained sample* ² $w_{\text{oxi.}}/\text{g}$	Composition of alloy* ³ (mass %)		
					Ca	Pt	O
					C_{Ca}	C_{Pt}	C_{O}
H	1.01 (52.6 mass%Ca)	1273	3	1.17 (1.22)	86.5	2.6	10.9
I	1.00 (42.2 mass%Ca)	1273	3	1.13 (1.17)	75.0	17.5	7.5
J	1.01 (52.6 mass%Ca)	1173	24	1.23 (1.22)	40.5* ⁴ 45.7	37.3* ⁴ 43.3	(22.2) 11.0
K	1.00 (42.2 mass%Ca)	1173	24	1.20 (1.17)	33.0* ⁴ 48.0	47.1* ⁴ 43.2	(19.9) 8.8

*1 Calcium content was determined by ICP analysis (cf. Table 2).

*2 Values in the lower line in parenthesis were calculated based on mass and composition of the alloy assuming the following reaction: Ca–Pt alloy + O₂ → CaO + Pt.

*3 Determined by EDS.

*4 Determined by ICP analysis.

Table 4 Results of dissolution experiments of platinum, Ca–Pt and oxidized sample.

Exp. #	Leaching sample	Leaching solution	Leaching time $t_{\text{Leach}}/\text{h}$	Mass of leaching sample	Mass of Pt in sample	Residue w_{res}/g	Mass of dissolved material	Mass of dissolved Pt* ¹	Mass % of dissolved Pt* ¹
				w_i/g	w_{Pt}/g		w_{sol}/g	w_{Pt}/g	C'_{Pt}
1.	Pt	HCl+ HNO ₃ * ²	4	0.103	0.103	0.082	0.021	0.014 (0.021)	13.7 (20.3)
2.	Ca–Pt	HCl+ HNO ₃	1	0.499	0.237	0.000	0.499	0.233 (0.237)	98.3 (100.0)
3.	Ca–Pt		1	0.504	0.291	0.000	0.504	0.295 (0.291)	101.2 (100.0)
4.	Oxidized sample	HCl+ HNO ₃	1	0.501	0.187	0.001	0.500	0.187 (0.187)	99.9 (99.8)
5.			1	0.508	0.239	0.006	0.502	0.237 (0.236)	98.9 (98.8)
6.	Pt	HCl* ³	4	0.103	0.103	0.100	0.003	0.000 (0.003)	0.0 (2.9)
7.	Ca–Pt	HCl	1	0.504	0.239	0.196	0.308	0.000 (0.146)	0.0 (61.1)
8.	Ca–Pt		1	0.495	0.286	0.276	0.219	0.000 (0.127)	0.0 (44.2)
9.	Oxide of Ca–Pt	HCl	1	0.505	0.188	0.050	0.455	0.146 (0.170)	77.3 (90.1)
10.	Oxide of Ca–Pt		1	0.499	0.235	0.107	0.392	0.132 (0.185)	56.0 (78.6)

*1 Values in parenthesis listed in the lower line are calculated from the mass of the dissolved sample and composition of the samples, and are listed for reference.

*2 Leached with mixture of 30 ml conc. HCl aq. and 10 ml conc. HNO₃ aq. at room temperature.

*3 Leached with 40 ml conc. HCl aq. at room temperature.

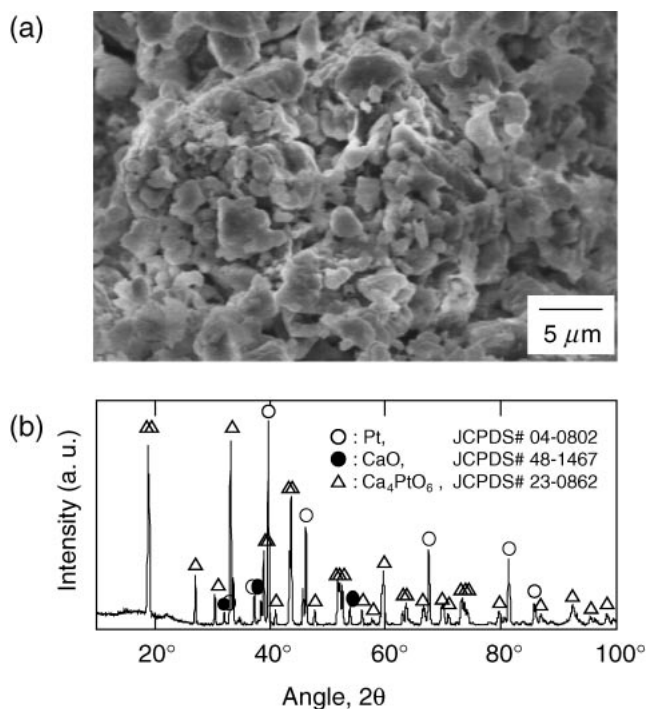


Fig. 7 (a) SEM image of Ca–Pt oxide and (b) XRD pattern of the obtained Ca–Pt oxide.

treatment followed by oxidation was found to be effective in increasing the ratio of dissolution of leaching with aqueous HCl. The increment of the ratio of dissolution in an aqueous HCl solution is probably due to the dissolution of Ca_4PtO_6 or of the complex platinum oxide formed after oxidation treatment.

Figure 8 shows SEM images of the platinum powder recovered from the residue after the leaching of the Ca–Pt alloy with HCl (*cf.* Exp. # 7 in Table 4). When the Ca–Pt alloy was dissolved in an aqueous HCl solution for one hour at room temperature, almost all the calcium in the alloy dissolved, and platinum grains with a large surface area and several micro cracks remained as residue.

The results of the leaching experiment are summarized in Fig. 9. The percentages of dissolved platinum after the leaching of pure platinum, Ca–Pt alloy, and oxidized samples in aqua regia or in an aqueous HCl solution at room temperature are also shown for comparison. The results in the figure clearly show that the Ca vapor treatment is effective in increasing the rate of dissolution in aqua regia. After the Ca vapor treatment, the platinum was completely dissolved when kept in aqua regia at room temperature for one hour, whereas only 14% of untreated platinum was dissolved when kept in aqua regia at room temperature for four hours. These results indicate that this method can be used in the pretreatment of scrap containing platinum because it is effective in increasing the dissolution rate. It is interesting to note that the rate of dissolution in aqueous HCl is high only in the case of the Ca–Pt alloy samples that have undergone the oxidation treatment. The details of the mechanism of dissolution by aqueous HCl are currently under investigation.

Figures 10(a) and (b) show an SEM image and an XRD pattern of hexachloroplatinate salt $(\text{NH}_4)_2\text{PtCl}_6$ powder recovered from Ca–Pt alloy, respectively. The precipitate

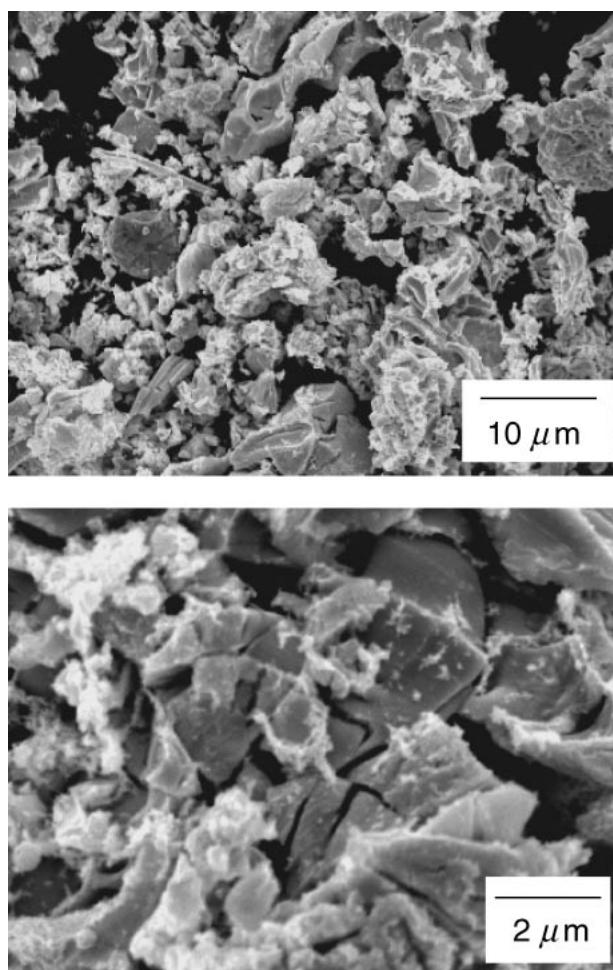


Fig. 8 SEM images of recovered Pt powder from the residue after leaching of the Ca–Pt alloy with HCl aq. solution.

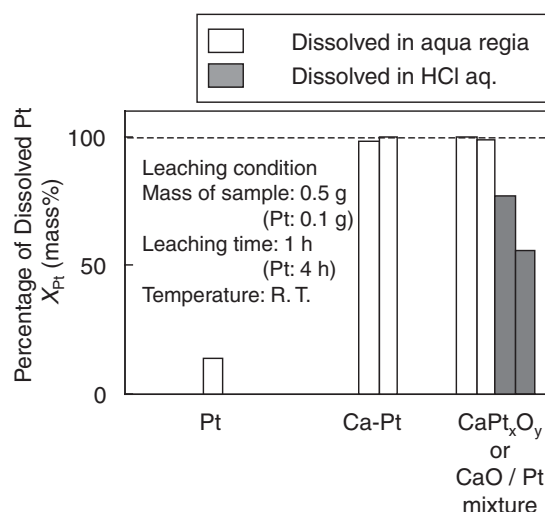


Fig. 9 Percentage of dissolved Pt after leaching Pt, Ca–Pt alloy or oxidized samples with aqua regia or HCl aq. solutions.

obtained from the leaching solution was a mixture of $(\text{NH}_4)_2\text{PtCl}_6$ and NH_4Cl , and contained no calcium compound. Figures 10(c) and (d) show an SEM image and an XRD pattern of platinum powder obtained from the $(\text{NH}_4)_2\text{PtCl}_6$ precipitate after the thermal decomposition

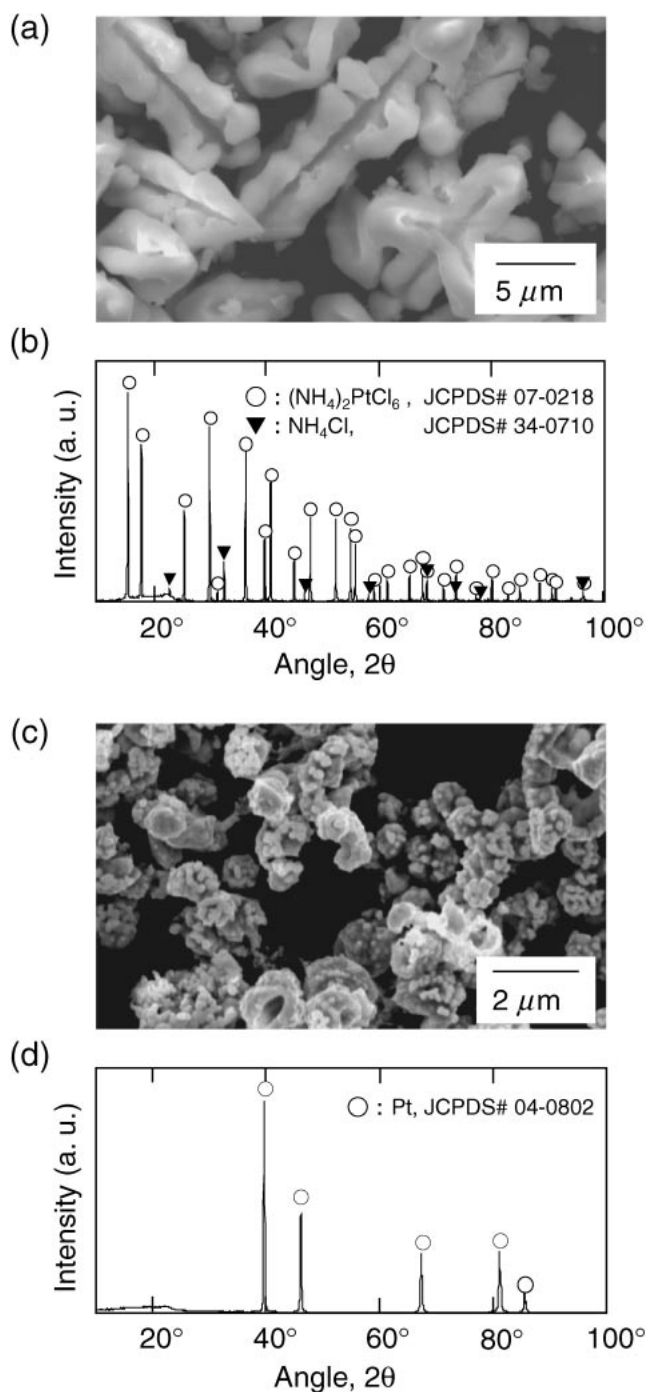


Fig. 10 (a), (b) SEM image and XRD pattern of $(\text{NH}_4)_2\text{PtCl}_6$ powder recovered from Ca–Pt alloy, and (c), (d) SEM image and XRD pattern of Pt powder obtained from $(\text{NH}_4)_2\text{PtCl}_6$ precipitate.

procedure. Pure platinum powder with grains less than 1 μm in diameter was obtained in this study.

The results of the experiment on the recovery of platinum from the Ca–Pt alloy are listed in Table 5. The symbols within brackets for each dissolution step correspond to the samples obtained at each step shown in Fig. 4. Platinum yields for each step are calculated on the basis of the mass of the obtained platinum, and the overall yield is calculated and listed for reference. The loss of platinum is chiefly due to filtration procedures, and therefore, the overall yield may be increased by improving the separation technique or by

Table 5 Results of the experiment on the recovery of platinum from the Ca–Pt alloy. Symbols in brackets for each dissolution step correspond to the samples obtained at each step shown in Fig. 4. The over all yield is calculated from recovered platinum, and yields for each step are also calculated and are listed in the same row for reference.

Starting metal	Ca–Pt alloy,	Mass of Pt in samples					Over all yield,*	
		Initial	[A]		[B]	[C]		[D]
			Pt in solution ^{&}	Sediment	After filtration ⁺	metallic powder		
		$w_{\text{alloy}}/\text{g}$	$w_{\text{init.}}/\text{g}$	w_{A}/g	w_{B}/g	w_{C}/g	w_{D}/g	$Y_{\text{all}} (\%)$
Ca–Pt	0.47	0.22	0.22	0.23	0.22	0.21		
			100	105	92	97		93
Ca–Pt	0.48	0.23	0.23	0.23	0.21	0.20		
			100	103	89	98		90
Ca–Pt	0.50	0.29	0.29	0.29	0.27	0.26		
			100	100	91	98		90
Ca–Pt	0.51	0.29	0.29	0.28	0.29	0.28		
			100	96	102	98		96

[&] Alloy samples were dissolved in aqua regia (30 ml conc. HCl aq. + 10 ml conc. HNO₃ aq.) at room temperature.

⁺ Filter loss: $w_{\text{loss}} = w_{\text{C}} - w_{\text{B}}$.

* $Y_{\text{all}} = 100 \times w_{\text{D}}/w_{\text{init.}}$.

enlarging the experimental scale. In a certain experimental condition, 96% of the platinum was recovered using the calcium vapor treatment, followed by aqua regia leaching.

4. Conclusion

A new platinum extraction process involving alloy formation using calcium vapor and successive leaching with an aqueous solution was investigated in this study. Pure platinum samples were reacted with calcium vapor at temperatures above 1073 K, and Ca–Pt alloy samples were synthesized. In some experiments, some of the obtained Ca–Pt alloys were oxidized in air to reduce the amount of acid necessary for dissolution. The obtained Ca–Pt alloy was dissolved in aqua regia at room temperature, and it was found that 100% of the platinum was dissolved in aqua regia at room temperature after the calcium vapor treatment, whereas only 14% of untreated pure platinum was dissolved in the same condition. It was found that the calcium vapor treatment was not effective in increasing the rate of dissolution in HCl at room temperature, but after oxidation more than 50% of the various samples was found to be dissolved, even in aqueous HCl solution. Platinum in the leaching solution was separated from the solution as $(\text{NH}_4)_2\text{PtCl}_6$ by precipitation, and pure platinum powder was obtained from the precipitate by thermal decomposition. It was found that more than 90% of the platinum was recovered by this process. This method can be applied in the pretreatment of scrap containing precious metals, because it is effective in increasing the rate of dissolution.

Acknowledgements

The authors are grateful to Prof. Yoshitaka Mitsuda at the University of Tokyo for his support and useful input during this study. Thanks are due to Messers Itaru Maebashi, Shusuke Iwata and Wataru Matsuno for experimental assistance.

REFERENCES

- 1) R. M. Heck and R. J. Farrauto: *Appl. Cat. A* **221** (2001) 443–457.
- 2) R. K. Mishra: *Proceedings of the 17th International Precious Metals Conference*, (International Precious Metals Institute, 1993) pp. 449–474.
- 3) F. E. Beamish: *Talanta* **5** (1960) 1–35.
- 4) L. M. Banbury and F. E. Beamish: *J. Fresenius' Z. Anal. Chem.* **2113** (1965) 178–187.
- 5) J. E. Hoffmann: *J. Met.* **406** (1988) 40–44.
- 6) G. H. Faye and P. E. Moloughney: *Talanta* **19** (1972) 269–284.
- 7) A. Diamantatos: *Anal. Chim. Acta* **94** (1977) 49–55.
- 8) Y. Kayanuma, T. H. Okabe and M. Maeda: *Collected Abstracts of the 2003 Autumn Meeting of the Japan Inst. Metals*, (2002) p. 396.
- 9) T. H. Okabe, S. Yamamoto, Y. Kayanuma and M. Maeda: *J. Materials Res.* (2003) in print.
- 10) F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen: *Cohesion in Metals: Transition Metal Alloys*, (North-Holland Physics Publishing, Elsevier Science Publishers B. V., Amsterdam, The Netherlands, 1989) pp. 624–625.
- 11) T. B. Massalski, ed.: *Binary Alloy Phase Diagrams*, (ASM, Metal Park, OH, 1986) pp. 633–634.
- 12) I. Barin: *Thermochemical Data of Pure Substances*, 3rd ed. (VCH Verlagsgesellschaft mbH, Weinheim, Federal Republic of Germany, 1995). p. 417, 1331.
- 13) A. Okuda and J. Shibata: *Shigen-to-Sozai (J. Mining and Materials Institute of Japan)*, **118** (2002) 1–8.