New extraction process of precious metals from scrap by chemical vapor treatment

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Abstract

A new process for extracting precious metals directly from scrap by chemical vapor treatment and successive leaching with an aqueous solution was investigated. Precious metals (M), particularly platinum (Pt), rhodium (Rh), and gold (Au), in plate or powder form were reacted with molten magnesium (Mg) at 1173 K for 12 h to synthesize Mg-M compounds. The obtained Mg-M compounds were then reacted with ferric chloride ($FeCl_3$) vapor at 673 K for 3 h to form complex chloride compounds. The chloride-treated samples were dissolved in hydrochloric acid (HCl aq.) or aqua regia. The dissolution efficiencies of Pt and Rh in aqua regia significantly increased after the treatment. This is probably due to the large surface area that is formed after the dissolution and removal of Mg from the compounds. On the other hand, although there was an increase in the surface area of the compounds, the dissolution efficiency of Au in the compounds was lower than that of pure Au. The method investigated in this study can be applied to the pretreatment of scrap that contains precious metals because it is effective both in increasing the dissolution efficiencies of Pt and Rh and in reducing the amounts of strong acids required for dissolution and waste solution.

1   Introduction

Precious metal (M) is the generic term for gold (Au), silver (Ag), and platinum-group metals (PGMs; platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru), and osmium (Os)). Since precious metals are characterized by excellent electric properties, high corrosion resistance, and heat resistance, they are widely used not only in jewelry but also in electronic parts, dental alloys, etc. In addition, PGMs are used in the automobile industry due to their various catalytic properties. The demand for PGMs is on the rise because of stricter environmental

regulations and the development of fuel cells. Although PGMs are gaining considerable importance, it is difficult to increase their production volume because not only are they rare and precious elements, but they also require copious amounts of energy and other resources for their extraction from mineral resources [1]. Moreover, their extraction and refining processes are accompanied by the generation of large amounts of waste.

In order to preserve these limited resources and reduce environmental burdens, it is extremely important to develop novel technologies for recovering precious metals from scrap. Typically, the recovery processes of precious metals are broadly classified as the pyrometallurgical process and the hydrometallurgical process. The pyrometallurgical process with high efficiency and speed is preferred in industries. However, it requires considerable amount of energy and large scale facilities. On the other hand, the hydrometallurgical process has the advantages of being operated under low energy cost and limited constraints of location requirements. Nevertheless, precious metals are chemically stable and barely dissolve in acids. Therefore, long processing time and considerable amounts of acids with strong oxidants are required for their dissolution. This results in the generation of a large amount of waste solution containing heavy metals and strong acids that is difficult to treat. However, if the dissolution characteristics of precious metals could be significantly improved to realize their dissolution in short time durations with small amounts of acids, a new energy saving recovery process for precious metals, which minimizes the generation of waste solution, can be established. For these reasons, the authors investigated a method for increasing the solubility of precious metals by chemical vapor treatment and aimed at developing a new environment-friendly extraction process.

Recently, a new extraction process using metal vapor treatment was developed by Okabe *et al*. [2-5]. In this process, precious metals, particularly Pt and Rh, were reacted with vapors of reactive metals (R) such as magnesium (Mg) or calcium (Ca). This process utilizes the chemical properties of PGMs, which have a strong affinity to reactive metals [6]. The obtained R-M compounds were dissolved in hydrochloric acid (HCl aq.) or aqua regia (a 3:1 mixture of concentrated HCl and HNO_3). During the course of the fundamental study [2-5], it was found that the dissolution efficiencies of Pt and Rh in aqua regia were significantly improved after the vapor treatment. Furthermore, the Ca-Pt compound oxidized in air was dissolved in HCl aq. without any oxidizing agent. In general, Pt metal is inert to HCl aq. in the absence of oxidants; however, reactive metal vapor treatment, followed by oxidation in air is found to be effective in dissolving the precious metals in HCl aq. without any strong oxidizing agent.

By considering the background mentioned above, the authors are currently investigating a new extraction process for precious metals, particularly Pt, Rh, and Au, by compound formation with reactive metals, followed by chlorination (or oxidation). Figure 1 shows a schematic representation of the change in the chemical potential of chlorine (or oxygen) with the processing time during the dissolution experiment. Considering Pt as an example, the conventional leaching process is shown in Fig. 1 (a), and the process investigated in this study is shown in Fig. 1 (b).

(a) Conventional leaching process

(b) Reactive metal treatment followed by chlorination (or oxidation)
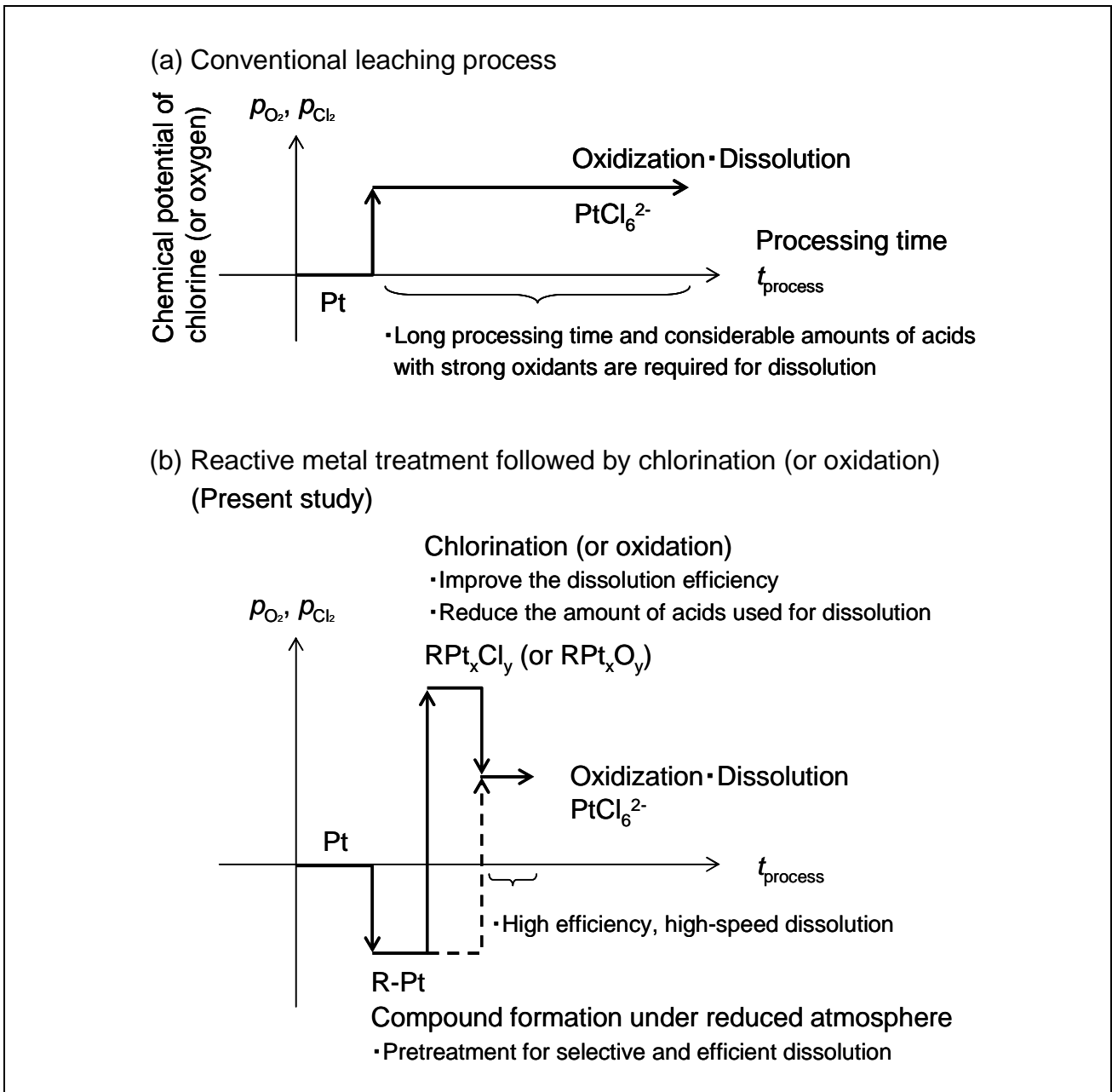(Present study)

Figure 1: Change of chlorine (or oxygen) chemical potential with processing time during dissolution experiment of platinum (schematic).
(a) Conventional leaching process using acids with strong oxidants.
(b) Reactive metal treatment followed by chlorination (or oxidation).

The process employed in this study is as follows: Pt is initially reacted with reactive metals in order to form compounds for achieving selective and effective dissolution. The synthesized R-Pt compounds are then chlorinated (or oxidized) to increase chlorine (or oxygen) potential and dissolve Pt in acids without oxidants. If an effective process which enables to dissolve precious metals using only HCl aq. is developed, discharge volume of waste solution containing heavy

metals and toxic acids can be reduced. In addition, if chloride wastes, such as $FeCl_x$ generated from the titanium (Ti) smelting process, can be effectively utilized as chlorine sources for chlorination, the disposal problem of chloride wastes can also be minimized.

In this study, Mg and ferric chloride ($FeCl_3$) are employed as the extraction medium and chlorination agent, respectively. Figure 2 shows the vapor pressure of selected metals and chlorides as a function of reciprocal temperature, calculated using the reference data [7]. When the vapor pressure of a chemical species exceeds 10^{-4} atm, it can easily be supplied and made to react with a target material (precious metals) in its vapor form. The advantage of supplying the mediums in vapor form is that vapor can be distributed into every corner of the scrap irrespective of its complicated structure. The vapor pressure of precious metals is more than a trillion (10^{15}) times smaller than that of reactive metals and iron chlorides; hence, the precious metals remain in the scrap during the compound formation process even at elevated temperatures.

By considering these properties, the authors have designed a new extraction process of precious metals by using reactive metals and chloride vapors as the reaction mediums; the effectiveness of this process was investigated through some fundamental experiments.
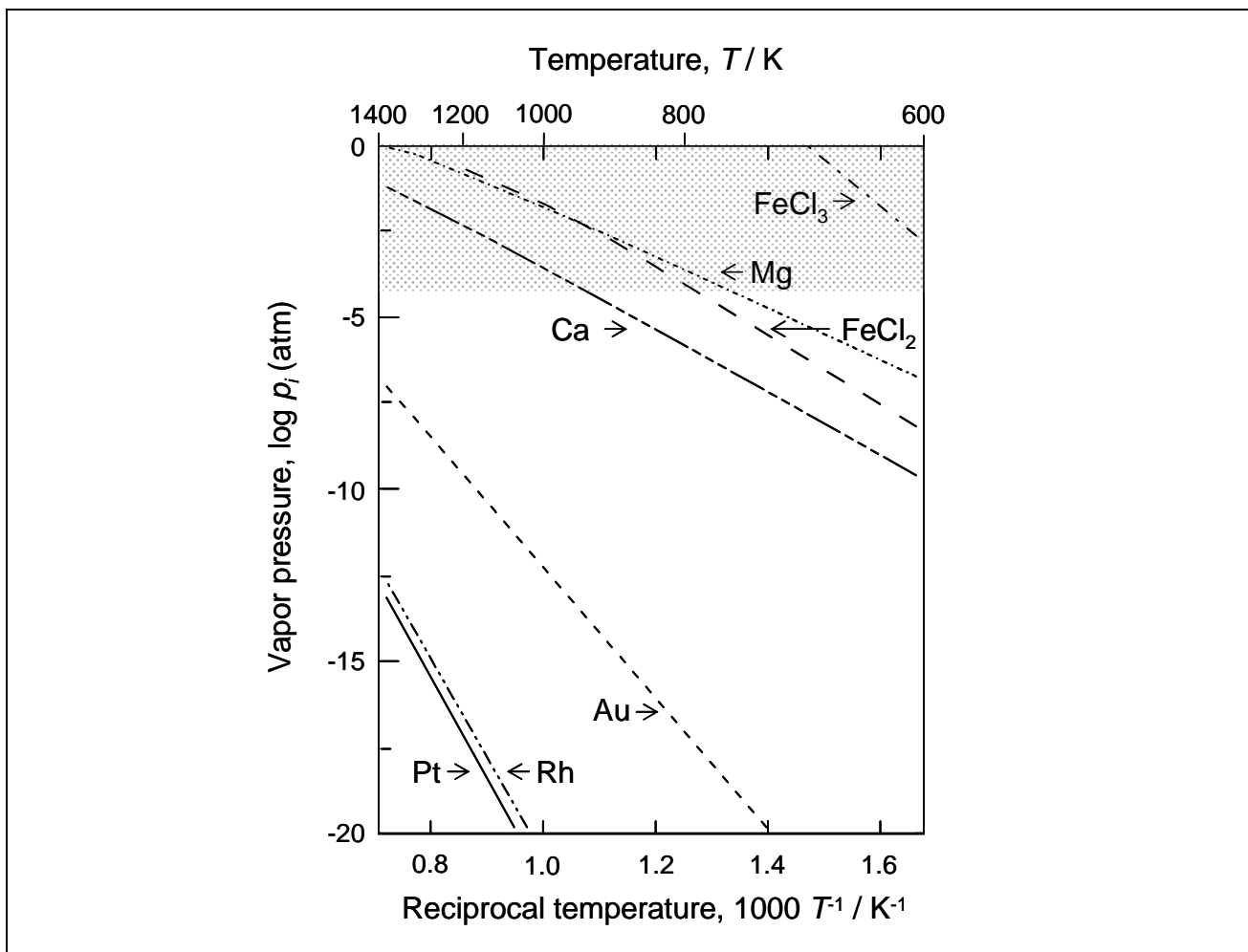

Figure 2:   Vapor pressure of selected metals and chlorides as a function of reciprocal temperature.

2   Experiment

Figure 3 shows the material flowchart of the extraction process of precious metals using reactive metals and chlorination agents as the reaction mediums. The process consists of four major steps: formation of R-M compound by R vapor treatment, chlorination (or oxidation), dissolution of compounds that contain precious metals by leaching with acids, and recovery of precious metals from the aqueous solution. In this study, the authors investigated the first three steps. First, the precious metals (M = Pt, Rh, and Au) were reacted with Mg and Mg-M compounds were synthesized. Next, the Mg-M compounds were reacted with $FeCl_3$ vapor to form complex chlorides. Finally, the chlorinated Mg-M compounds were dissolved in HCl aq. or aqua regia.
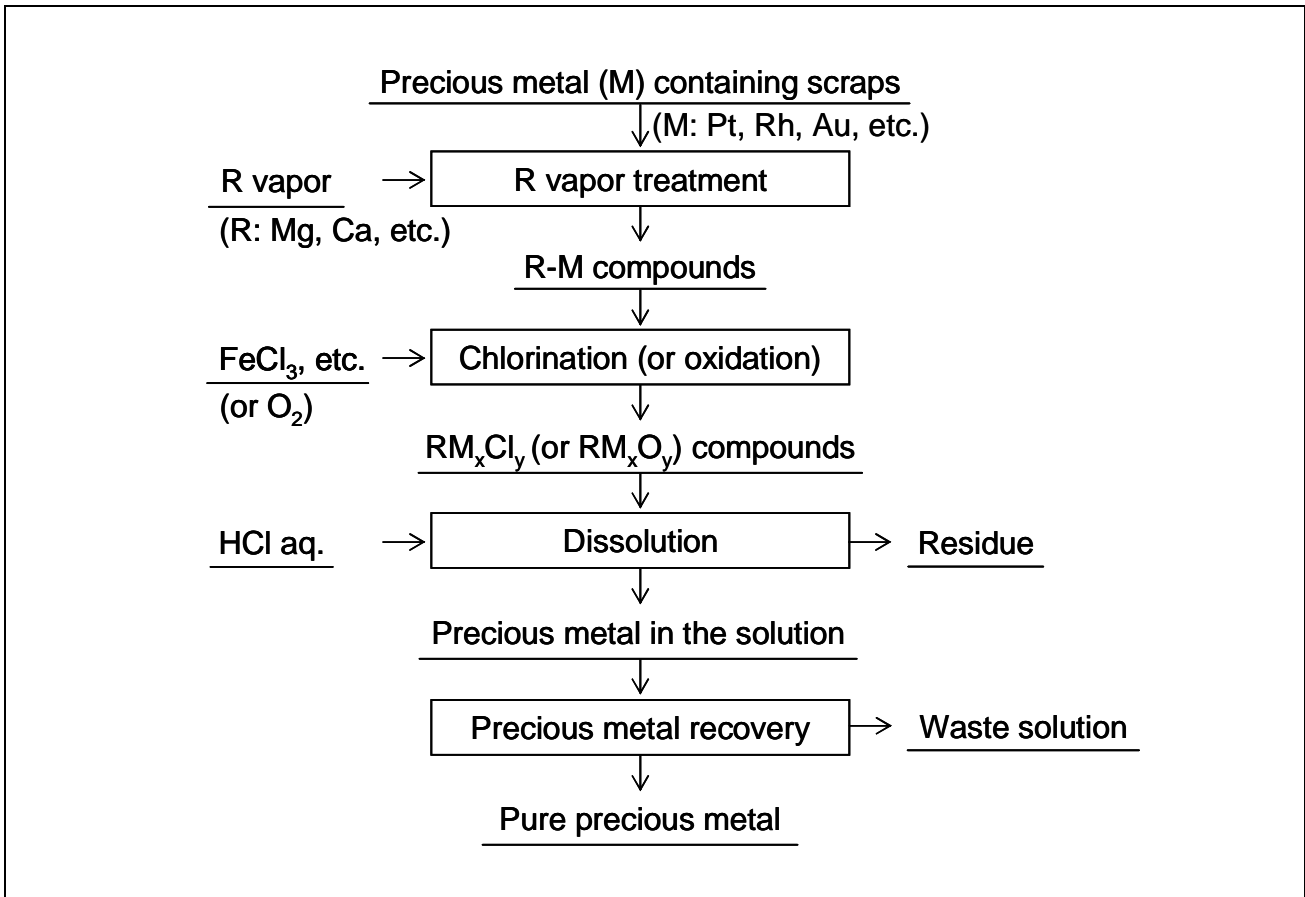

Figure 3:   Recovery process of precious metals involving complex chloride (or oxide) formation by chloride vapor treatment.

2.1 Synthesis of Magnesium-precious metal Compounds

A schematic illustration of the experimental apparatus used for the synthesis of Mg-M compounds is shown in Fig. 4. Two to five grams of plates (0.5-0.6 mm thick) or powders (diameters of 0.5 μm) of precious metals (M = Pt, Rh, and Au) and Mg lumps (1-6 g) were loaded into a tantalum (Ta) crucible, which was installed in a thick-walled stainless steel reaction vessel. The vessel was sealed by tungsten inert gas (TIG) welding. Sponge titanium was also placed at the bottom of the vessel for the gettering of nitrogen (N_2) gas in the system.

The sealed reaction vessel was then heated in an electric furnace maintained at 1173 K for 12 h. After the experiment, the reaction vessel was removed from the furnace and quenched into water. The sample in the vessel was mechanically recovered at room temperature and was subjected to the following chlorination and leaching processes.
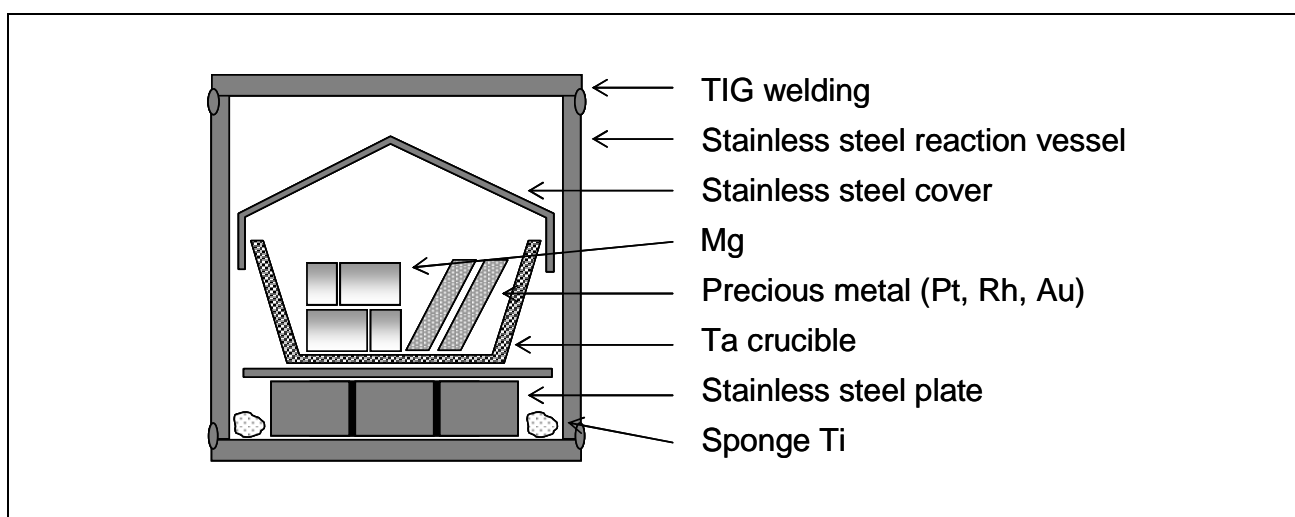

Figure 4: Schematic illustration of the experimental apparatus used for the synthesis of the Mg-precious metal compounds.

2.2 Chlorination of the Magnesium-precious metal Compounds

Figure 5 shows a schematic illustration of the experimental apparatus used for the chlorination of the Mg-M compounds. Approximately 0.5 g of the obtained Mg-M compounds was crushed in a mortar and classified by sieving, and the powder with particle diameter less than 600 μm was placed in a quartz crucible (I.D.   = 18 mm). Precious metal powder was also placed in a quartz crucible for reference. Chlorinating agent, $FeCl_3$ (3-4 g), was placed in a stainless steel crucible. Using a stainless steel sample holder, these crucibles were loaded in a stainless steel reaction vessel (I.D.   = 35 mm, length = 120 mm). This stainless steel reaction vessel was inserted into a quartz tube (I.D.   = 40 mm, length = 455 mm), and the samples were reacted at 673 K for 3 h under an

argon atmosphere. The chlorinating agent, $FeCl_3$, was supplied in its vapor form in order to react with Mg-M compounds because the vapor pressure of $FeCl_3$ at 673 K exceeds beyond 10^{-4} atm [7]. After the experiment, the samples in the quartz crucibles and the deposits in the quartz tube and stainless steel reaction vessel were recovered and subjected to analysis.
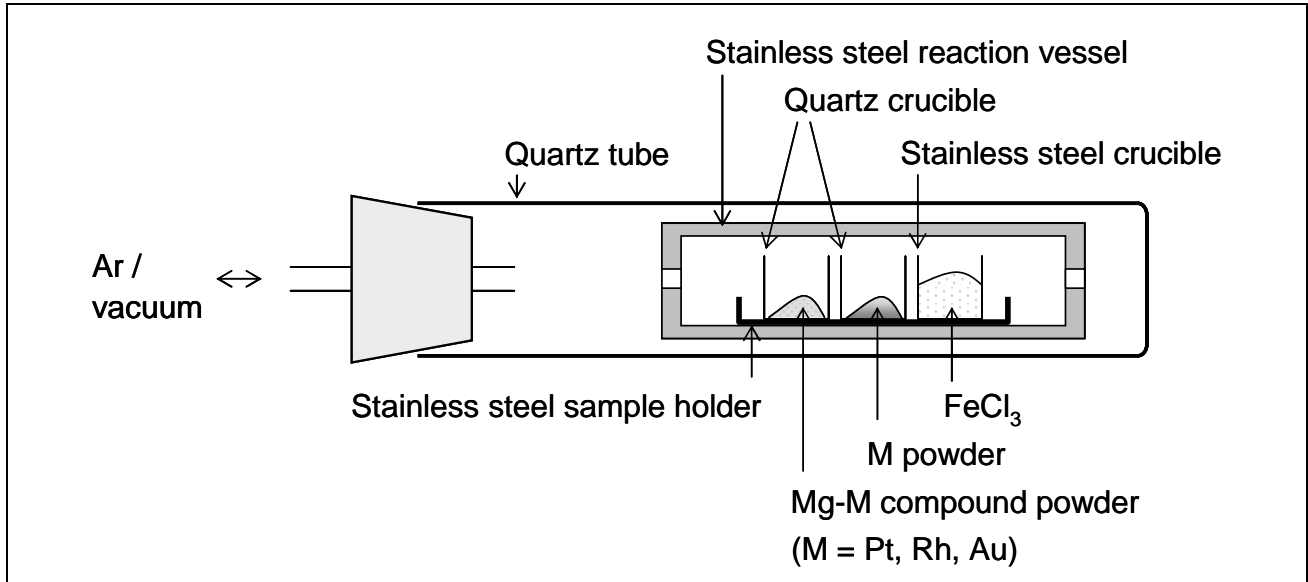

Figure 5: Schematic illustration of the experimental apparatus for the chlorination of the Mg-precious metal compound.

2.3 Dissolution of the Chlorinated Magnesium-precious metal Compounds

The obtained Mg-M compounds and chlorinated samples were dissolved in HCl aq. or aqua regia at 293-333 K for 1 h. For each 0.1 g of the sample, 40 ml of concentrated HCl aq. or aqua regia was used for dissolution. After dissolving the samples, the solid residues in the leaching solution were filtrated using filter paper (pore size of 0.03 μm). The residues were then subjected to analysis.

2.4 Analysis

The morphology of the obtained solid samples was observed by scanning electron microscopy (SEM), and their composition was determined by energy-dispersive X-ray spectroscopy (EDS) and X-ray fluorescence (XRF) analysis. Phases in the samples were identified by X-ray diffraction (XRD) analysis.

3   Results and Discussion

3.1 Synthesis of the Magnesium-precious metal Compounds

Table 1 lists a few representative experimental conditions and corresponding results of the Mg-M compound formation. Figure 6 shows the SEM images of the compounds that were obtained after crushing them mechanically in a mortar. The SEM/EDS analysis showed that homogeneous compounds were obtained. Identification of the phases in the sample was attempted by the XRD analysis; however, the phases could not be identified because the XRD patterns of the sample did not correspond with that of the reference data.

Table 1:   Experimental conditions for the synthesis of Mg-M compounds and analytical results of the obtained compounds.[a]

Exp. #	Precious metal,	Mass of M,	Mass of Mg,	Mass of obtained compound,	Composition of compound (mass%)[b]				
	M	w_M / g	w_{Mg} / g	w_{comp} / g	Mg	Pt	Rh	Au	O
1a	Pt	4.99	4.12	6.65	37.67	43.80	—	—	18.53
2a	Rh	5.00	6.10	10.06	43.84	—	43.37	—	12.79
3a	Au	5.00	1.25	5.34	27.37	—	—	26.97	45.66

a: Reaction temperature, $T = 1173$ K, reaction time, $t'' = 12$ h.
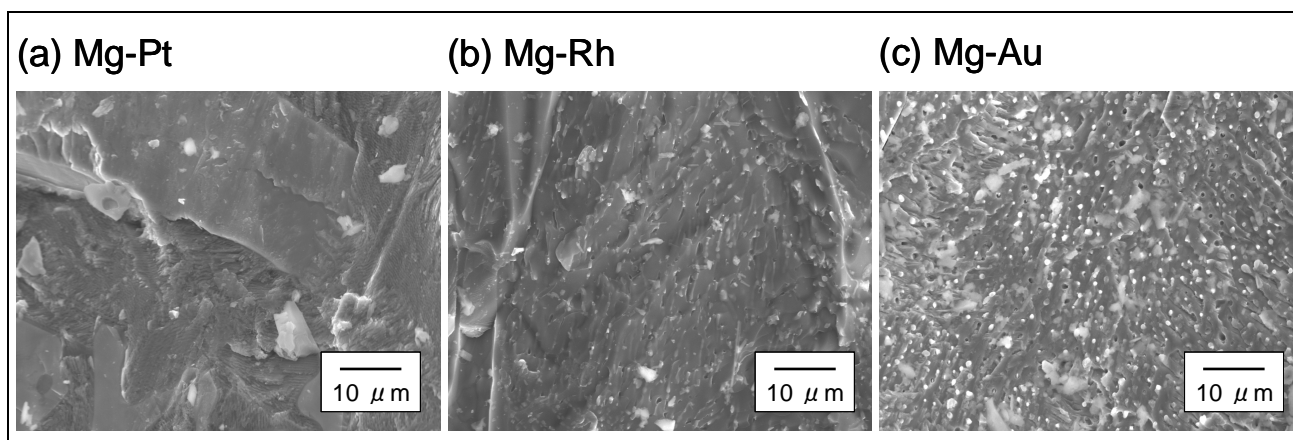b: Values determined by EDS analysis.
—: Not analyzed.

Figure 6:   SEM images of the Mg-M compounds synthesized for the leaching experiment.
(a) Mg-Pt, (b) Mg-Rh, and (c) Mg-Au.

3.2 Chlorination of the Magnesium-precious metal Compounds

The experimental results of chlorination are summarized in Table 2. After chlorination was carried out using $FeCl_3$ vapor, the increase in the mass of Mg-M compounds was larger than that of the precious metals. Identification of the phases present in the chlorinated samples by the XRD analysis was difficult due to the absence of corresponding reference data.

Table 2: Experimental conditions for the chlorination experiments of synthesized Mg-M compounds and analytical results of the obtained compounds.[a]

Exp. #	Feed material	Mass of feed material [b], w_{mat} / g	Mass of feed $FeCl_3$, w_{FeCl_3} / g	Mass of obtained sample [c], w_{chlo} / g	Composition of sample (mass%)[d]					
					Mg	Pt	Rh	Au	Fe	Cl
1b	Pt	0.501	3.980	0.510	—	59.24	—	—	6.71	34.05
2b	Mg-Pt	0.499		0.601	2.46	29.05	—	—	24.60	43.89
3b	Rh	0.499	2.997	0.534	—	—	—	—	31.06	68.94
4b	Mg-Rh	0.501		0.776	1.69	—	—	—	49.22	49.09
5b	Au	0.442	3.003	0.442	—	—	—	63.50	12.55	23.95
6b	Mg-Au	0.500		0.616	1.91	—	—	22.07	31.48	44.54

a: Reaction temperature, T = 673 K, reaction time, t'' = 3 h.
b: Feed material M or Mg-M compounds (M = Pt, Rh, and Au).
c: Material obtained after the chlorination experiment.
d: Values determined by XRF analysis.
—: Not analyzed.

3.3 Dissolution of the Chlorinated Magnesium-precious metal Compounds

Tables 3 and 4 summarize the results of the dissolution experiments performed in HCl aq. and aqua regia, respectively. The dissolution results of pure precious metals and chlorinated precious metals are also listed for comparison. The ratios of dissolved precious metals after the leaching experiments are summarized and shown in Fig. 7. Figure 7 clearly shows that the dissolution efficiencies of Pt and Rh in aqua regia from the Mg-M and chlorinated Mg-M compounds, were significantly enhanced, and their dissolution ratio reached a maximum of 100 mass%. On the contrary, the dissolution ratio of Au in aqua regia from the Mg-Au and chlorinated Mg-Au

compounds, was reduced to one tenth of that of pure Au, while pure Au dissolved completely under the same condition. The reason for these results is currently being investigated. Although precious metals in chlorinated Mg-M compounds were not dissolved in HCl aq., it was found that chlorination does not interfere with the dissolution of Pt and Rh in aqua regia. It is noteworthy that reactive metal treatment and chlorination have an influence on the dissolution efficiency during leaching with an acid. However, a more detailed experimental work, including confirmation of reproducibility, is required for discussing the dissolution mechanism.

Table 3: Results of the dissolution experiments of M, Mg-M, and chlorinated Mg-M compounds in HCl aq.[a]

Exp. #	Leaching sample	Mass of leaching sample, w_i / g	Mass of M in sample, w_M / g	Residue, w_{res} / g	Mass of dissolved material [c], w_{sol} / g	Mass of dissolved M [d], w_d / g	Mass% of dissolved M [e], C'_M (%)
1c	Pt	0.101	0.101	0.091	0.010	0.010	9.9
2c	Mg-Pt	0.099	0.043	0.052	0.047	0.000	0.0
3c	Mg-Pt-FeCl$_3$	0.101	0.031	0.045	0.056	0.000	0.0
4c	Pt-FeCl$_3$	0.101	0.061	0.089	0.012	0.000	0.0
5c	Rh [b]	0.101	0.101	0.090	0.011	0.011	10.9
6c	Mg-Rh [b]	0.099	0.043	0.043	0.056	0.000	0.0
7c	Mg-Rh-FeCl$_3$ [b]	0.100	0.028	0.026	0.074	0.002	7.1
8c	Rh-FeCl$_3$ [b]	0.101	0.094	0.083	0.018	0.011	11.7
9c	Au	0.099	0.099	0.099	0.000	0.000	0.0
10c	Mg-Au	0.101	0.027	0.090	0.011	0.000	0.0
11c	Mg-Au- FeCl$_3$	0.101	0.022	0.071	0.030	0.000	0.0
12c	Au- FeCl$_3$	0.098	0.061	0.093	0.005	0.000	0.0

a: Dissolution temperature, T = RT (room temperature, 293-298 K), reaction time, t'' = 1 h, leached using 40 ml of concentrated HCl solution.

b: Dissolution temperature, T = 323-333 K.

c: Calculated from the change in mass of the sample, $w_{sol} = w_i - w_{res}$.

d: Calculated from the change in mass of the sample, $w_d = w_M - w_{res}$.

e: Calculated from the mass of precious metals in the sample before and after leaching, $C'_M = (w_d / w_i) \times 100$.

Table 4:   Results of the dissolution experiments of M, Mg-M, and chlorinated Mg-M compounds in aqua regia.[a]

Exp. #	Leaching sample	Mass of leaching sample, w_i / g	Mass of M in sample, w_M / g	Residue, w_{res} / g	Mass of dissolved material [c], w_{sol} / g	Mass of dissolved M [d], w_d / g	Mass% of dissolved M [e], C'_M (%)
1d	Pt	0.100	0.100	0.091	0.009	0.009	9.0
2d	Mg-Pt	0.099	0.043	0.000	0.099	0.043	100.0
3d	Mg-Pt-FeCl$_3$	0.100	0.031	0.000	0.100	0.031	100.0
4d	Pt-FeCl$_3$	0.099	0.059	0.083	0.016	0.000	0.0
5d	Rh [b]	0.100	0.100	0.090	0.010	0.010	10.0
6d	Mg-Rh [b]	0.094	0.041	0.000	0.094	0.041	100.0
7d	Mg-Rh-FeCl$_3$ [b]	0.100	0.028	0.000	0.100	0.028	100.0
8d	Rh-FeCl$_3$ [b]	0.100	0.093	0.080	0.020	0.011	14.0
9d	Au	0.099	0.099	0.000	0.099	0.099	100.0
10d	Mg-Au	0.099	0.027	0.025	0.074	0.002	7.4
11d	Mg-Au- FeCl$_3$	0.101	0.022	0.019	0.082	0.003	13.6
12d	Au- FeCl$_3$	0.100	0.062	0.000	0.100	0.062	100.0

a: Dissolution temperature, T = RT (room temperature, 293-298 K), reaction time, t'' = 1 h, leached using 40 ml of concentrated HCl solution.

b: Dissolution temperature, T = 323-333 K.

c: Calculated from the change in mass of the sample, $w_{sol} = w_i - w_{res}$.

d: Calculated from the composition and change in mass of the sample with the assumption that precious metals are the last to dissolve, $w_d = w_M - w_{res}$.

e: Calculated from the mass of precious metals in the sample before and after leaching, $C'_M = (w_d / w_i) \times 100$.
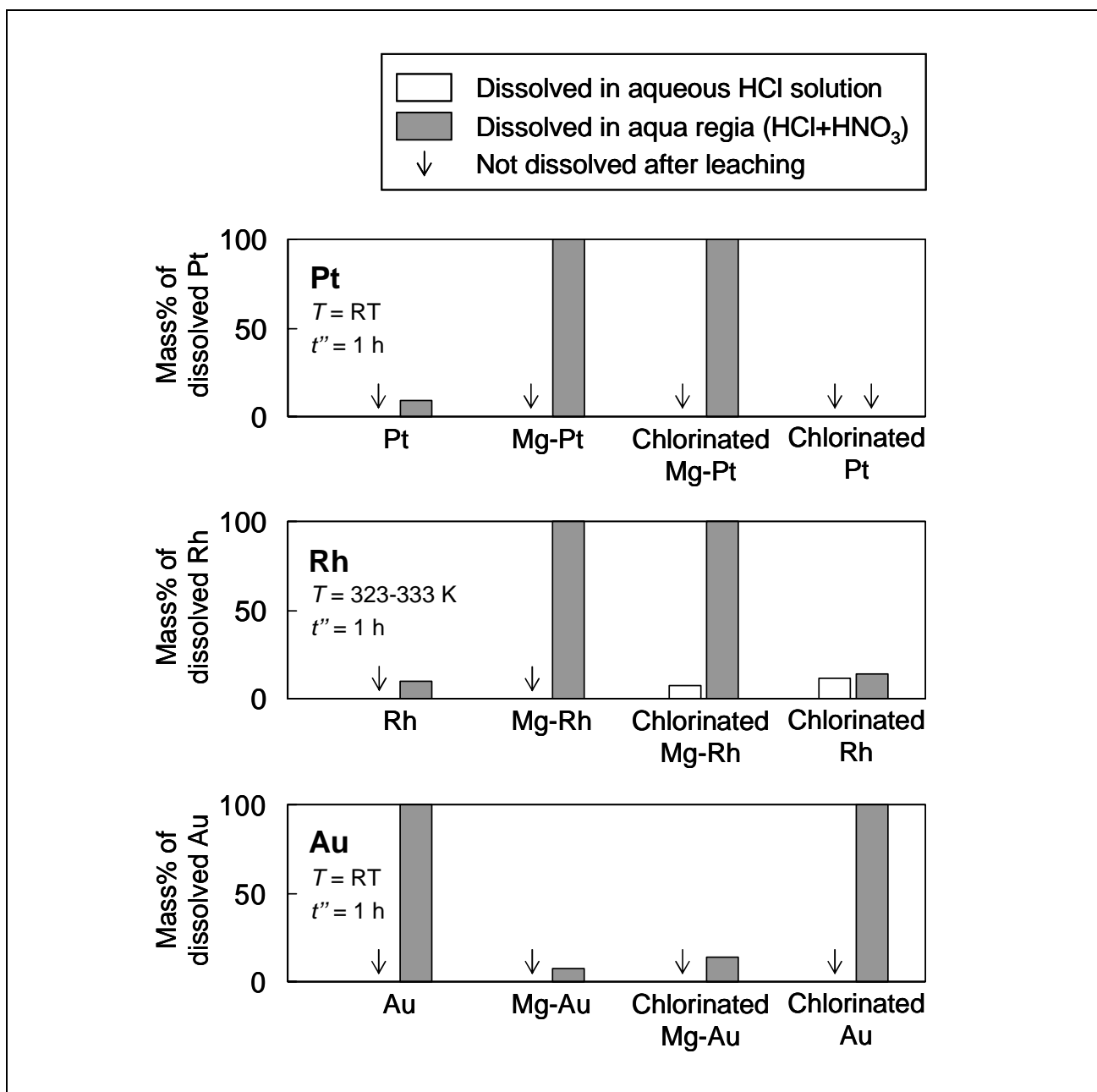
Figure 7: Percentage of dissolved precious metals (M = Pt, Rh, and Au) after the leaching experiment. Pure M, Mg-M compounds, and chlorinated samples were reacted with HCl aq. or aqua regia.

Figure 8 shows the SEM images of the residues obtained after the leaching experiment. The experiment was performed in HCl aq. for 1 h using chlorinated Mg-M compounds. In each sample, Mg and Fe from the compounds were dissolved, and their mass ratio became less than 1 mass%. Grains of precious metals with several microcracks were obtained as residues. The increase in the dissolution efficiencies of Pt and Rh from the Mg-M and chlorinated Mg-M compounds is probably due to the large surface area formed after/during the dissolution of Mg in the compounds. Similar to the Pt and Rh systems, the surface area of Au that was obtained after the leaching experiment increased. However, the dissolution efficiency of Au in aqua regia from the Mg-Au and chlorinated Mg-Au compounds, reduced between 7% and 14%, although that of pure Au was 100% under the same condition. The authors are currently investigating the reason for this reduction in the dissolution efficiency.
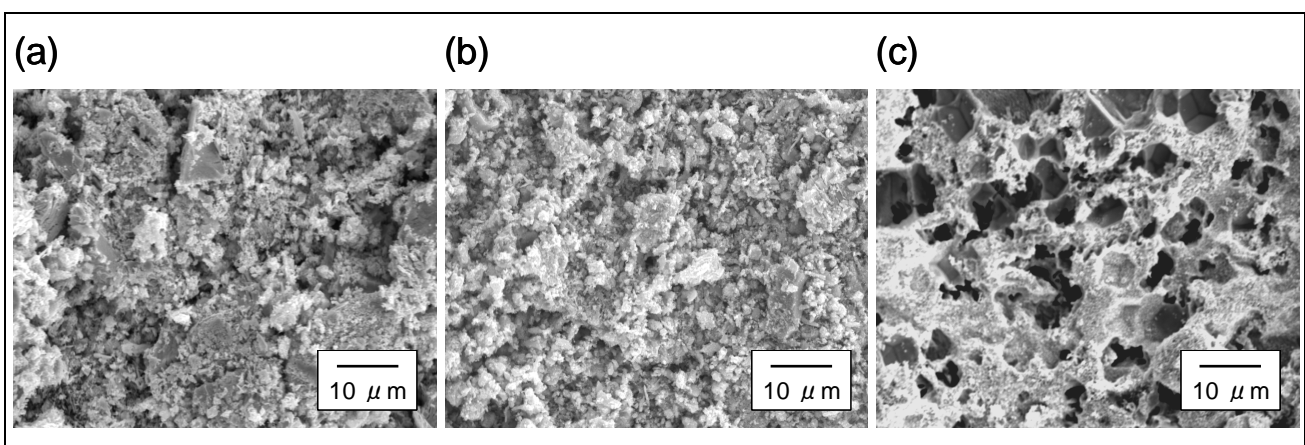

Figure 8:   SEM images of recovered precious metals from the residue obtained after leaching with HCl aq. Starting sample: (a) chlorinated Mg-Pt, (b) chlorinated Mg-Rh, and (c) chlorinated Mg-Au compounds.

4   Conclusion

A new extraction process of precious metals involving the formation of Mg-M compounds, followed by chlorination and leaching with an acid was investigated in this study.

Pure precious metals were reacted with molten Mg to synthesize Mg-M compounds. The obtained compounds were then chlorinated using $FeCl_3$ vapor. The Mg-M compounds and chlorinated samples were dissolved in HCl aq. or aqua regia. The mass% of dissolved Pt and Rh in aqua regia from the Mg-M and chlorinated Mg-M compounds, reached 100%, whereas those of pure Pt and Rh were only 10% under the same condition. On the contrary, the mass% of dissolved Au in aqua regia from the Mg-Au and chlorinated Mg-Au compounds, became one tenth of that of pure Au. In the case of HCl aq., only Mg or/and Fe from the Mg-M compounds or from the chlorinated samples was dissolved, and grains of precious metals with several microcracks were obtained as residues. It was found that the surface areas of the obtained residues were greater than those of pure precious

metals leached under the same condition. This resulted in an increase in the dissolution efficiencies of Pt and Rh in aqua regia from the Mg-M and chlorinated Mg-M compounds. However, a different mechanism is involved in the dissolution of Au in aqua regia from the Mg-Au and chlorinated Mg-Au compounds. The reason for this mechanism is currently under investigation.

The authors are currently investigating the new extraction process using other reactive metals and chlorides for compound formation. If a process that can dissolve precious metals using acids without oxidants is established, a new environment-friendly extraction process of precious metals would be available.

Acknowledgments

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