New Separation and Recovery Process of Platinum using Chlorinating Agents

Chiyoko Horike and Toru H. Okabe

Institute of Industrial Science
The University of Tokyo, Japan
Platinum group metals (PGMs)

Characteristics
- High electric conductivity
- Corrosion resistance
- Heat resistance
- Catalytic properties

The worldwide demand for Pt is increasing.

The development of an efficient recovery process of Pt is very important.

http://www.platinum.matthey.com/market_data/1147696728.html
Previous research conducted by our group

New extraction process of PGMs from waste materials by using reactive metal vapor

Alloying treatment of PGMs using reactive metals vapor

The dissolution efficiency of PGMs in aqua regia improved significantly.

Pourbaix diagram for Pt-H\textsubscript{2}O-Cl system

Pt is dissolved in 1M HCl to form a chloro complex in the +4 oxidation state.

The chlorination of Pt is an effective pretreatment for dissolution.
Purpose of this study

Development of a new process for the effective recovery of PGMs from scrap

Chlorination

- Higher dissolution efficiency
- Lesser amounts of acids required for dissolution
- Fast dissolution

Chemical potential of chlorine $p_{Cl_2}$

Processing time, $t_{\text{process}}$

R: reactive metal

Compound formation under a highly reducing atmosphere
- Pretreatment for selective and efficient dissolution of PGMs
Flowchart of the new process

Scrap containing PGMs (M) (M: Pt, etc.)

- Mg vapor treatment

Mg vapor treatment

Mg-M compounds

Chlorination

Mg-R'-M-Cl compounds

Dissolution

Solution containing PGMs

PGMs recovery

Pure PGMs

Waste solution

Residue

Reactive metal (Mg)

Chlorinating agent (Cl₂ or R’Clₓ)

(R’Clₓ: FeCl₃, CuCl₂, etc.)

HCl aq.
Pure Pt was reacted with molten Mg at 1173 K for 12 h. Homogeneous Mg-Pt compounds were formed. (SEM, EDS, XRD)
Chlorination of Mg-Pt compounds and Pt

Feed samples were chlorinated by using a chlorinating agent (Cl₂, FeCl₃, or CuCl₂ gas) at 673 or 873 K for 3 h.

- Reaction at 673 K

Weight of the feed samples: 0.32–0.40 g
- Cl₂: 10 g
- KMnO₄: 10 g
- conc. HCl: 40 ml
- FeCl₃: 3.68–4.05 g
- CuCl₂: 3.31–3.99 g

Chlorinating agent (FeCl₃ or CuCl₂)
Compounds obtained after chlorination

After chlorination in CuCl$_2$ at 673 K and 873 K for 3h

Mg-Pt compound powder

Pure Pt powder

The morphologies and colors of the samples were different.
Weight measurement

Comparison of weight change

Effective chlorinating condition:
(1) Mg-Pt compound
(2) High temperature (873 K was more effective than 673 K)
(3) Chloride salts
XRD analysis

Chlorination agent: CuCl\textsubscript{2}
Reaction temperature: 873 K

The sample obtained after chlorination was different from the feed Mg-Pt.

However, their phases were not identified.
### Composition analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analysis</th>
<th>Composition of element $i$, $C_i$ (mass%)</th>
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<tbody>
<tr>
<td></td>
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*Not detected

**Cu of CuCl_2 participated in this chlorination.**
Summary

A fundamental technique that utilizes the selective alloying of PGMs using collector metals followed by chlorination/oxidation.

1. Pt was reacted with Mg at 1173 K and the obtained Mg-Pt compounds were “chlorinated” by using the vapors of a chlorinating agent (Cl₂, FeCl₃, or CuCl₂) at 673 K and 873 K.

2. During chlorination, Pt was effectively reacted with chloride salts at 873 K after Mg alloying. After the experiment, Pt formed a complex compound.

Future work:
Integration of the proposed chlorination method with the conventional dissolution methods of chlorinated Pt in acid solution will be investigated.
New Separation and Recovery Process of Platinum using Chlorinating Agents

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# The Price of PGMs

<table>
<thead>
<tr>
<th>Metal</th>
<th>US$ per g</th>
<th>US$ per kg</th>
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<tr>
<td>Pt</td>
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<tr>
<td>Pd</td>
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<td>11,061.09</td>
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<tr>
<td>Rh</td>
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<td>Os</td>
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<td>Au</td>
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<td>Ag</td>
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<td>Cu</td>
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<td>Al</td>
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**Johnson Matthey Base Prices**

- 16 Feb 2007
- 8:30 (Hong Kong Time)

**GFMS London Fixings**

- am 15 Feb 2007
- [http://www.gfms.co.uk/spot_prices.htm](http://www.gfms.co.uk/spot_prices.htm)

**LME Official Price**

- 15 Feb 2007
- [http://www.lme.co.uk/dataprices_daily_metal.asp](http://www.lme.co.uk/dataprices_daily_metal.asp)
Supply and Demand

Supply

<table>
<thead>
<tr>
<th>Country</th>
<th>Pt 205 t</th>
<th>Pd 235 t</th>
<th>Rh 23 t</th>
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<td>29 t (12%)</td>
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<tr>
<td>South Africa</td>
<td>159 t (78%)</td>
<td>81 t (34%)</td>
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<td>Russia</td>
<td>27 t (13%)</td>
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<tr>
<td>Other</td>
<td>8 t (4%)</td>
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<td>3 t (12%)</td>
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<td>Russia</td>
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<td>19 t, 83%</td>
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Demand

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<td>Chemical</td>
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<tr>
<td>Auto catalyst</td>
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<td>94 t (44%)</td>
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<td>Jewelry</td>
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<td>21 t (84%)</td>
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<tr>
<td>Other</td>
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<td>9 t (4%)</td>
<td>0.5 t (2%)</td>
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<tr>
<td>South Africa</td>
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<td>North America</td>
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http://www.platinum.matthey.com/market_data/1132069464.html
Typical recovery process for PGMs

Scraps containing PGMs

Pre-treatment (Crushing, etc.)

Collector metal containing PGMs

Dissolution in acid

Separation and purification

Recovered PGMs

Pyrometallurgical process
- High efficiency
- High speed
- High energy cost
- Large-scale facilities required

Hydrometallurgical process
- Low energy cost
- Easy handling
- Long processing time
- Generation of a large amount of waste solution

Cu, Pb, Fe, etc.

Extraction by collector metals

Directly dissolved in acid
Pt recovery process by precipitation of (NH$_4$)$_2$PtCl$_6$

R-Pt compounds or Pt

Chlorination

Chloride complex containing Pt

Dissolution

Solution containing Pt

NH$_4$Cl aq. → Crystallization

S → L

(NH$_4$)$_2$PtCl$_6$

Calcination / Reduction

Pt powder

Waste solution

HCl, NH$_3$, etc.
Rose process

Crushing

Automotive catalyst scrap

Crushing

Smelting (1573 - 1673 K, 4 h)

Air or O$_2$

Cu metal

Slag

Smelting

Cu$_2$O

Cu metal

PGM recovery

PGMs

Fig. PGMs recovery process from automotive catalyst scrap.

*Laid-open disclosure public patent bulletin H04-317423 (1992).*
Ellingham diagram

Vapor pressure of selected metals and chlorides

![Graph showing vapor pressure of selected metals and chlorides](image)

- **Pt**, **Fe**, **Cu**, **CuCl**, **FeCl₂**, **FeCl₃**, **Mg**, **MgCl₂**

- **Temperature ranges:**
  - **873 K**
  - **673 K**

- **Axes:**
  - **Vapor pressure, log \( p \), (atm)**
  - **Reciprocal temperature, 1000 \( T^{-1} \) / K⁻¹**
The predicted enthalpy of formation

\[ \Delta H_{\text{calc}}^{\text{for}} / \text{kJ} \cdot \text{mol}^{-1} \]

\begin{align*}
\text{Mg-Pt} & : \text{Pt}_2\text{Mg}_3, \text{PtMg}, \text{Pt}_3\text{Mg}_2, \text{Pt}_2\text{Zn}_3, \text{PtZn}, \text{Pt}_3\text{Fe}_5, \text{Pt}_2\text{Fe}_3, \text{PtFe}, \text{Pt}_3\text{Fe}_2, \\
\text{Zn-Pt} & : \text{PtCu}, \text{Pt}_3\text{Cu}_5, \text{Pt}_2\text{Cu}_3, \text{PtCu}, \text{Pt}_3\text{Cu}_2
\end{align*}

Phase diagram of Mg-Pt binary system
Chlorination using Cl$_2$ gas

The reaction setup includes:
- Ar gas flow (Ar)
- Chlorine gas inlet (Cl$_2$ gas inlet)
- Chlorination reactor
- Powder of Mg-Pt compound or Pt
- Dehydrator
- Conc. KMnO$_4$ aq.
- Conc. HCl aq.
- H$_2$O bubbler
- P$_2$O$_5$
- Light-proof bubbler
- Conc. KMnO$_4$ aq.
- Na$_2$S$_2$O$_3$ aq.
- Gas outlet (Heater)
- Cl$_2$ absorber
XRD analysis

The obtained sample from Mg-Pt compounds
Chlorination by Cl₂

\[ T = 673 \text{ K} \]
XRD analysis

The obtained sample from Mg-Pt compounds Chlorination by FeCl₃

\[ T = 673 \, \text{K} \]

- Pt #04-0802
## Composition analysis

Chlorination agent: CuCl₂  
Reaction temperature: 673 K

<table>
<thead>
<tr>
<th>Sample</th>
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*Not detected
## Composition analysis

**Chlorination agent:** FeCl₃  
**Reaction temperature:** 673 K

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<th>Analysis</th>
<th>Composition of element $i$, $C_i$ (mass%)</th>
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<td><strong>Feed MgPt</strong></td>
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### Composition analysis

Chlorination agent: FeCl$_3$

Reaction temperature: 873 K

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<th>Analysis</th>
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<td>Mg</td>
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<tr>
<td>Feed MgPt</td>
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*Not detected
# Composition analysis

Chlorination agent: Cl₂  
Reaction temperature: 673 K

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<td>Mg</td>
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<td>Feed MgPt</td>
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## Composition analysis

**Chlorination agent:** Cl\(_2\)

**Reaction temperature:** 873 K

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