

New Extraction Process of Precious Metals from Scrap by Chemical Vapor Treatment

Chihiro Ohkawa
Toru H. Okabe

Institute of Industrial Science
The University of Tokyo, Tokyo, Japan

New Extraction Process of Precious Metals from Scrap by Chemical Vapor Treatment

1. Introduction

- Background
- Previous research
- Purpose of this study

2. Experimental

3. Results

4. Summary

Precious metals

| | IA | IIA | IIIA | IVA | VA | VIA | VIIA | VIII | | IB | II B | IIIB | IVB | VB | VIB | VII B | 0 | |
|---|---------------------|---------------------|----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------------------|---------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
| 1 | H 1.01 | | | | | | | | | | | | | | | | | He 4.00 |
| 2 | Li 6.94 | Be 9.01 | | | | | | | | | | | B 10.81 | C 12.01 | N 14.01 | O 16.00 | F 19.00 | Ne 20.18 |
| 3 | Na 23.00 | Mg 24.31 | | | | | | | | | | | Al 26.98 | Si 28.09 | P 30.97 | S 32.07 | Cl 35.45 | Ar 39.95 |
| 4 | K 39.10 | Ca 40.08 | Sc 44.96 | Ti 47.89 | V 50.94 | Cr 52.00 | Mn 54.94 | Fe 55.85 | Co 58.93 | Ni 58.69 | Cu 63.55 | Zn 65.39 | Ga 69.72 | Ge 72.61 | As 74.92 | Se 78.96 | Br 79.90 | Kr 83.80 |
| 5 | Rb 85.48 | Sr 87.62 | Y 88.91 | Zr 91.22 | Nb 92.91 | Mo 95.94 | Tc [99] | Ru 101.07 | Rh 102.91 | Pd 106.42 | Ag 107.87 | Cd 112.41 | In 114.82 | Sn 118.71 | Sb 121.76 | Te 127.60 | I 126.90 | Xe 131.29 |
| 6 | Cs 132.91 | Ba 137.33 | * 57~71 | Hf 178.49 | Ta 180.95 | W 183.84 | Re 186.21 | Os 190.23 | Ir 192.22 | Pt 195.08 | Au 196.87 | Hg 200.59 | Tl 204.38 | Pb 207.21 | Bi 208.98 | Po [210] | At [210] | Rn [222] |
| 7 | Fr [223] | Ra [226] | ** 89~103 | Unq [261] | Unp [262] | Unh [263] | Uns [262] | Uno [265] | Une [266] | | | | | | | | | |

http://www.hkairnet.ne.jp/shung/periodic_table_s.htm


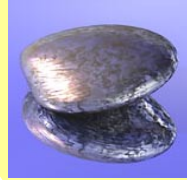


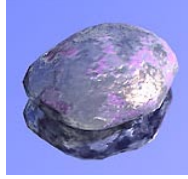
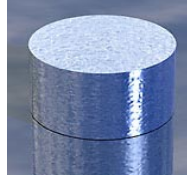


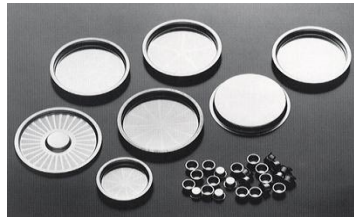
| | | | |
|---|--|---|--|
| 44 Ruthenium (Ru)  | 45 Rhodium (Rh)  | 46 Palladium (Pd)  | 47 Silver (Ag)  |
| 76 Osmium (Os)  | 77 Iridium (Ir)  | 78 Platinum (Pt)  | 79 Gold (Au)  |
| Platinum group metals (PGMs) | | | |

Fig. Periodic table and photographs of precious metals.

Precious metals

Chemical industry (Pt, Pd, Ru, Au, etc.)

- Textile industry



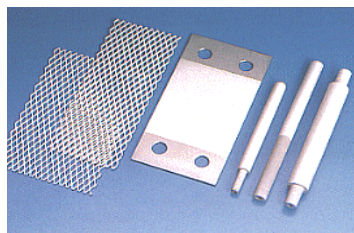
http://www.nippon-nz.com/japanese/jigyo/pdct_220.html

- Thermocouples



<http://www.ishifuku.co.jp/Products/Industrial/intro7.htm>

- Infusible electrodes



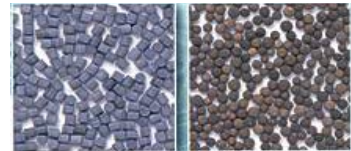
<http://www.ishifuku.co.jp/Products/Industrial/intro7.htm>

Catalysts (Pt, Pd, Rh, etc.)

- Automotive exhaust catalyst

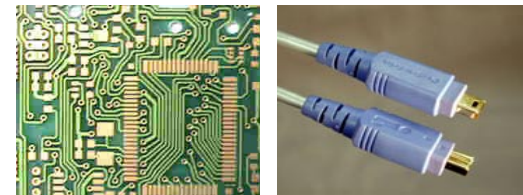


- Petrochemical industry



<http://www.ne-chemcat.co.jp/kagaku/noblemetal/index.html>

Semiconductors, electronic components (Au, Ag, Pd, Ru, etc.)



<http://www.kkmisuzu.co.jp/>

<http://www.users-side.co.jp/catalog/>

Laboratory instruments (Pt, Ir, Au, etc.)

(Pt, Ir, Au, etc.)



<http://www.inter-g7.or.jp/tanaka/products/products.html>

Dental alloys (Au, Pt, Pd, etc.)



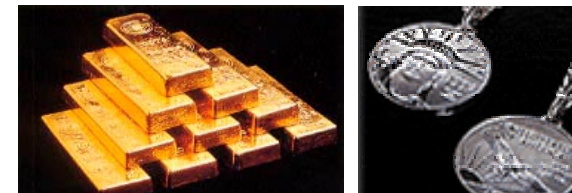
<http://www.tokuriki-kanda.co.jp/shika/index.html>

Jewelry (Au, Pt, Ag, Rh, etc.)



<http://www.ishifuku.co.jp/Jewelry/>

Assets, investments (Au, Pt, etc.)



<http://www.mki.co.jp/mitsuiPR/memberlist/kinzoku/kinzoku3.htm>

<http://www.tanaka.co.jp/eagle/eagle02.html>

Supply and demand

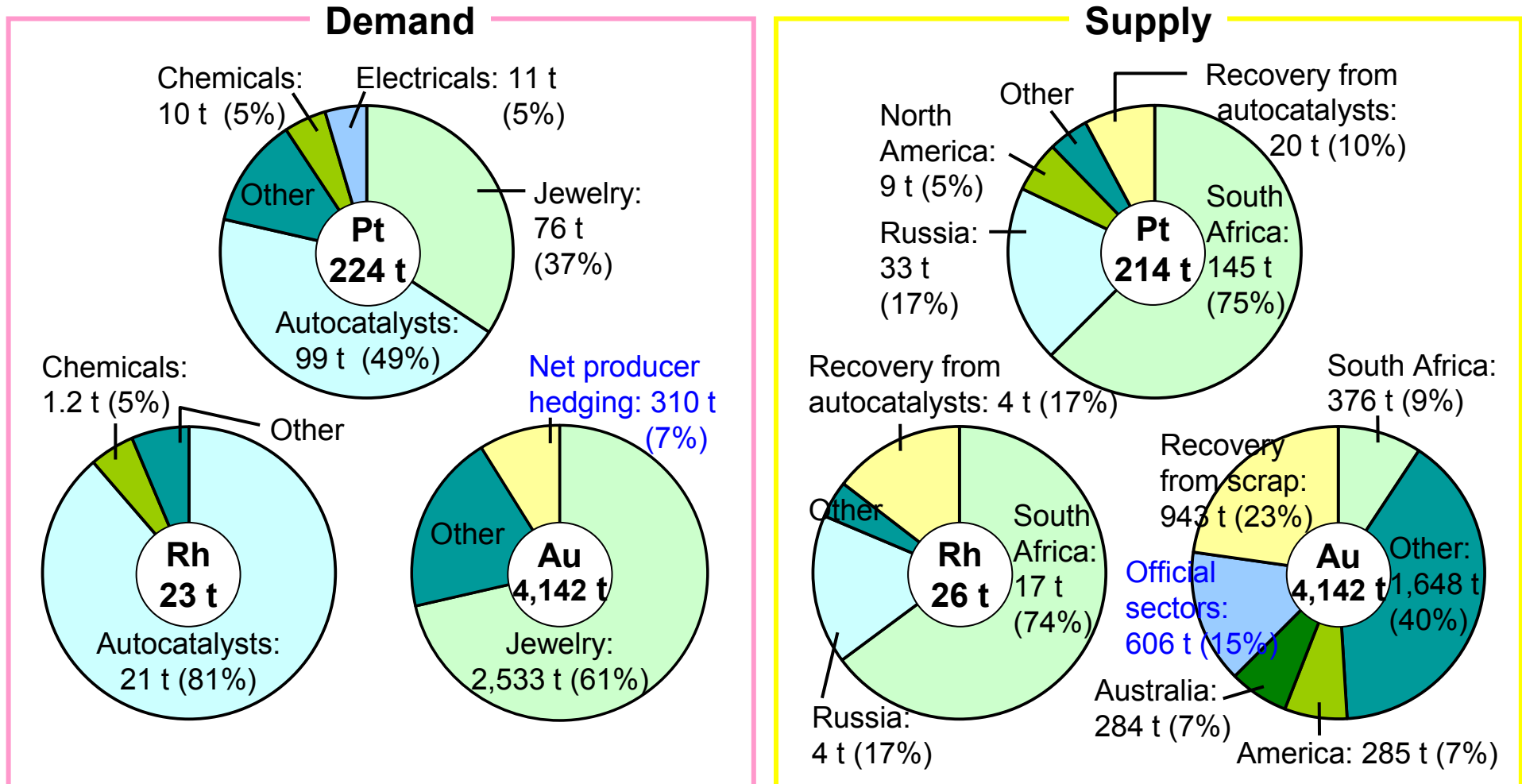


Fig. Supply and demand of precious metals in the world (2003).

*Johnson Matthey PLC: *Platinum 2004* (2004).

**Gold Fields Mineral Services Ltd.: *Gold Survey 2004* (2004).

Transition and prediction of Pt demand

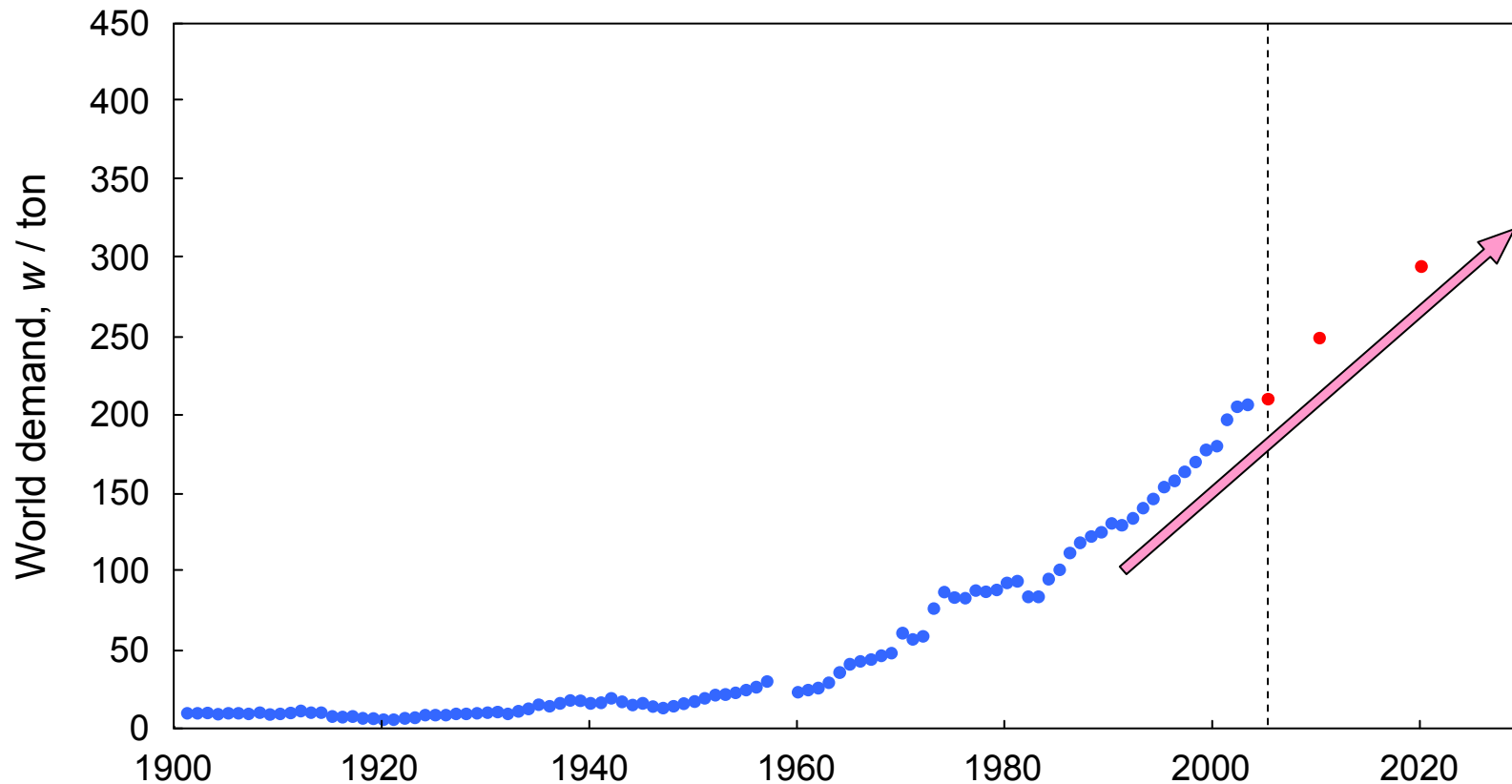


Fig. Transition and prediction of world demand of platinum from 1900 to 2030.

The demand for Pt is increasing because of tightening environmental regulations.
The development of fuel cells may also increase the Pt demand.

Typical recovery process for precious metals

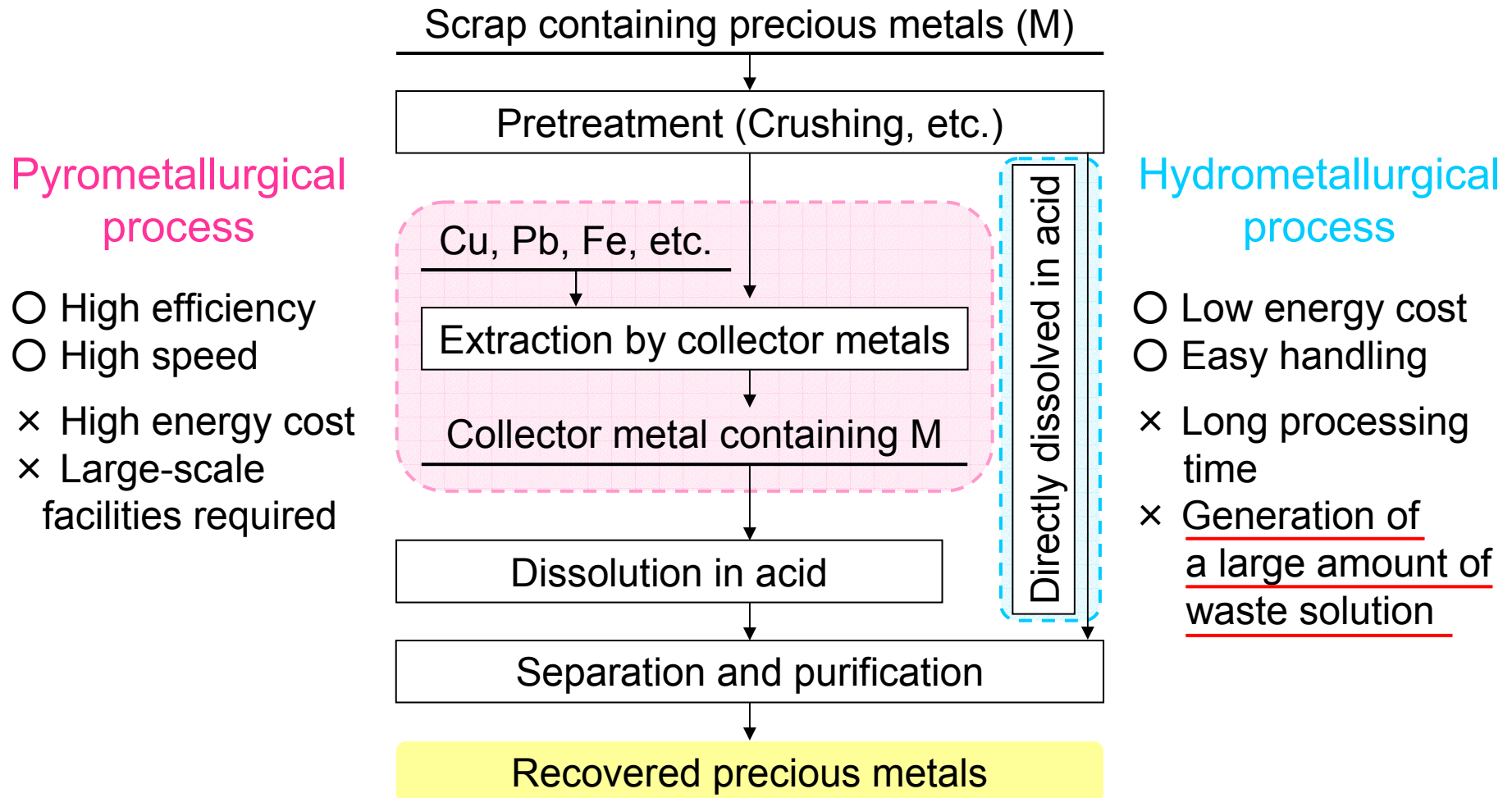
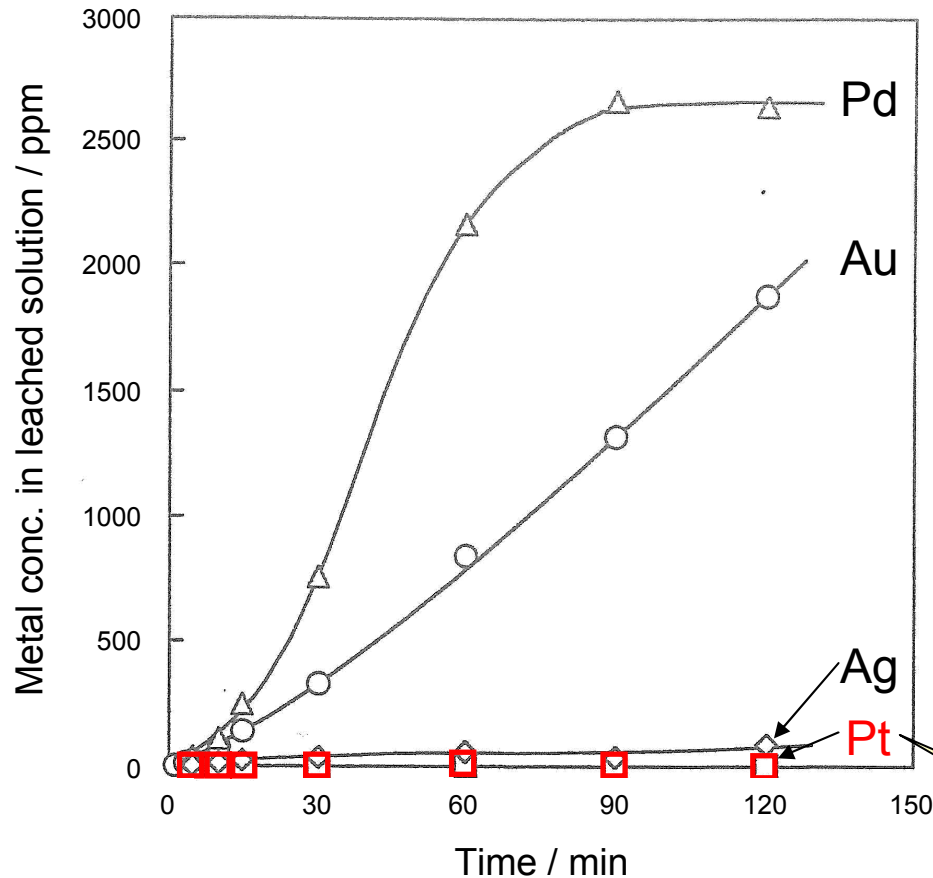


Fig. Typical recovery process for precious metals from scrap.

Dissolution rate of precious metals



Dissolution of precious metals is very difficult, even by aqua regia.

Hydrometallurgical process requires a large amount of acid with a strong oxidant and involves a long processing time.

→ If dissolution efficiency of precious metals is increased, hydrometallurgical process is expected to transform into a new energy saving process.

Leaching rate of Pt is extremely low.

Fig. Dissolution behaviors of Au, Ag, Pt, and Pd with aqua regia as a function of time. (Solution volume: 300 cm³. Sample form: 10 x 10 x 0.5 mm (1.07 g), Leaching temperature: RT)

Previous research

New extraction process for PGMs from waste materials
by using reactive metal (R = Mg, Ca, etc.) vapor

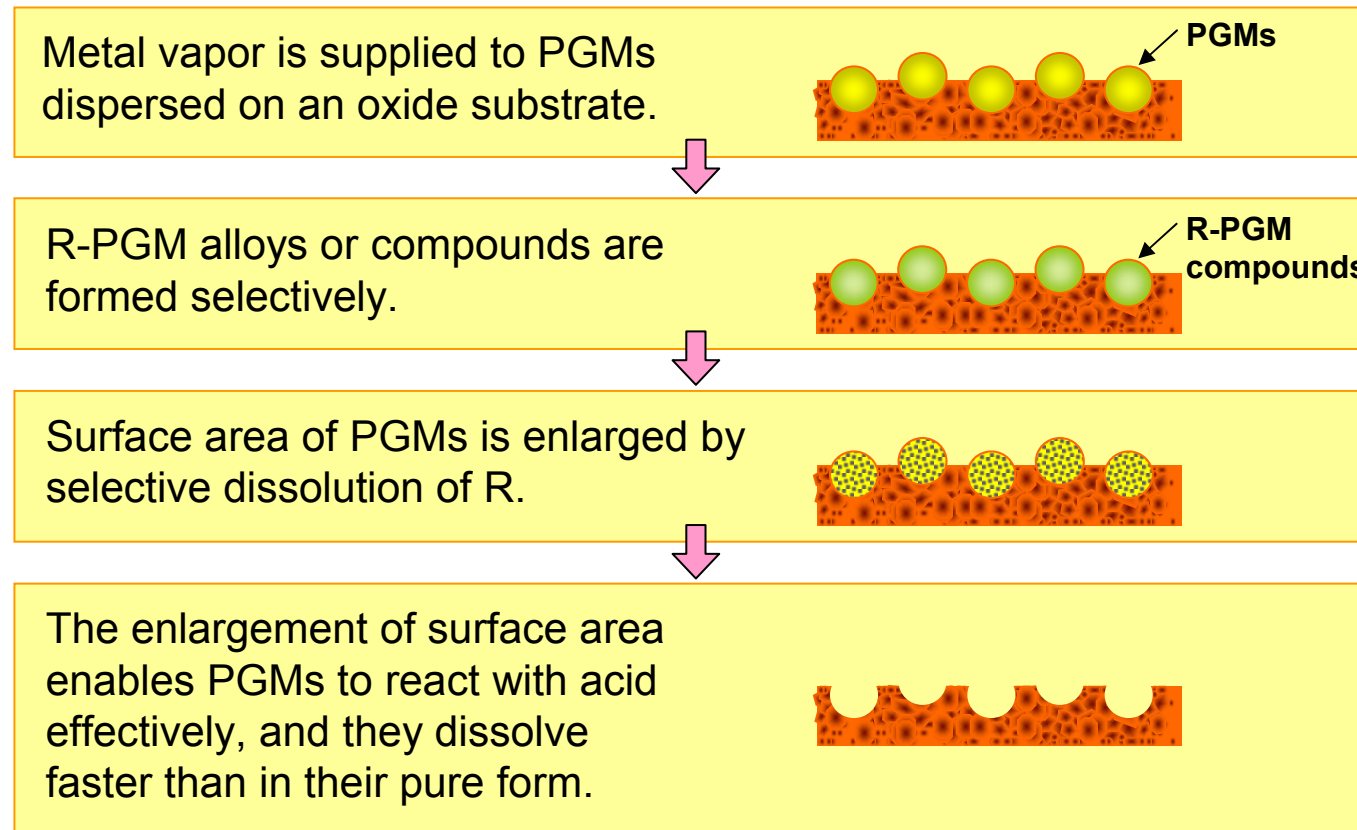


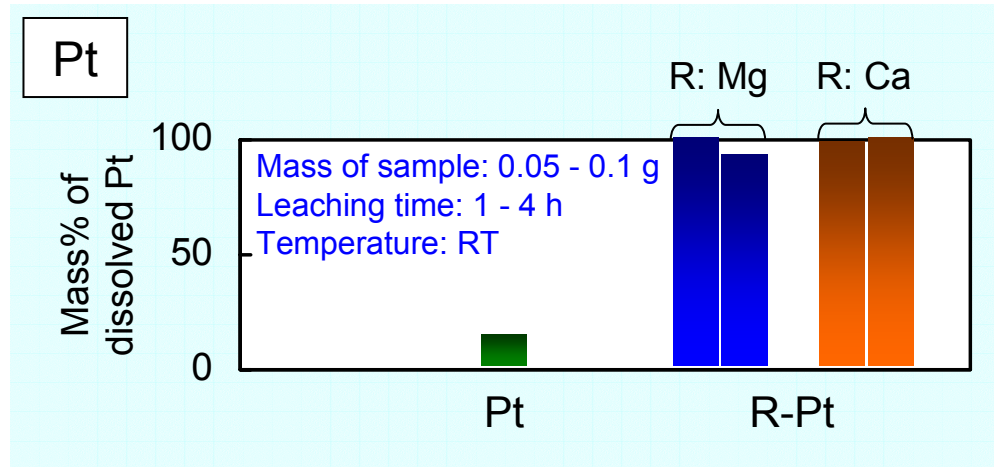
Fig. Concept of the metal vapor treatment of PGMs in waste materials.

*T. H. Okabe et al., Journal of Materials Research, **18**, No. 8 (2003), pp. 1960–1967.

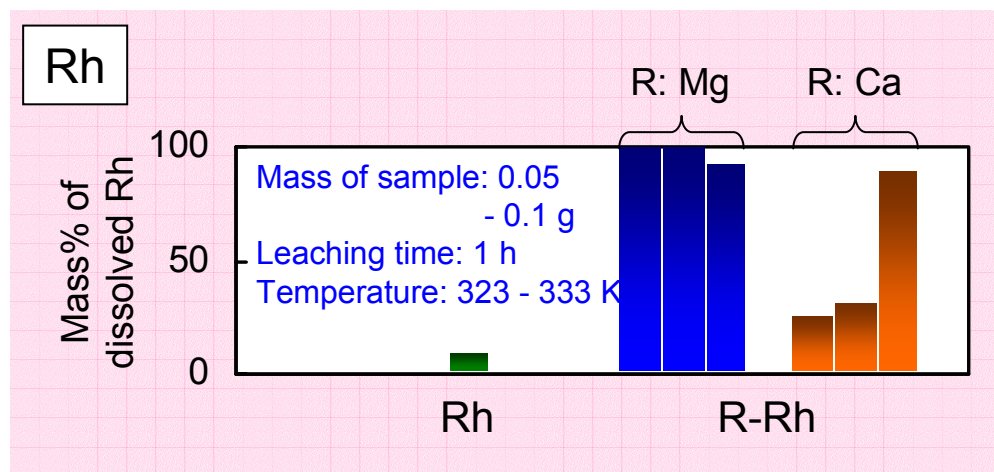
T. H. Okabe et al., Materials Transactions, JIM, **44, No. 7 (2003), pp. 1386–1393.

***Y. Kayanuma et al., Journal of Alloys and Compounds, **365** (2004), pp. 211–220.

Previous research



Mg or Ca treatment of pure Pt or Rh was effective in enhancing the dissolution rate of Pt and Rh in aqua regia.



However, there still remains a problem: the generation of a large amount of waste solution containing heavy metals and strong acids.

Fig. Results of dissolution experiments of R-Pt and R-Rh samples using aqua regia.

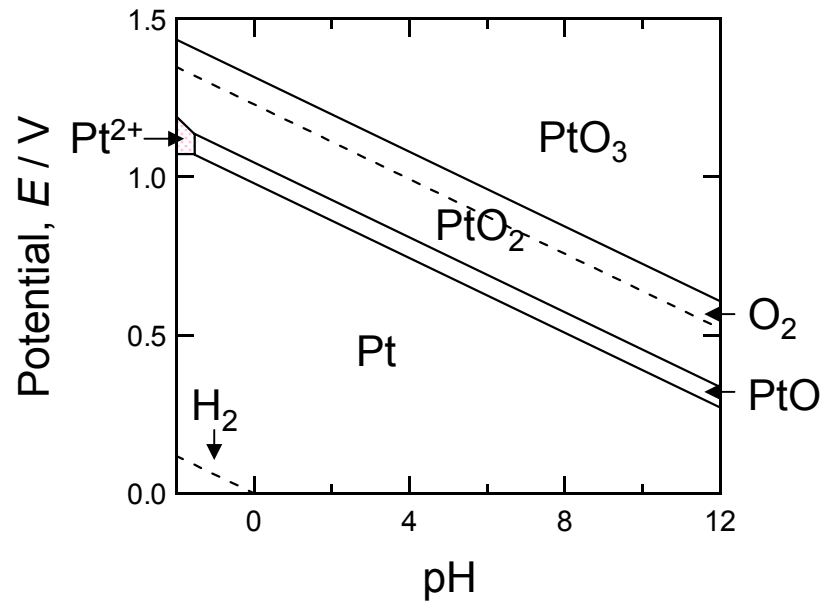
*T. H. Okabe et al., Journal of Materials Research, **18**, No. 8 (2003), pp. 1960–1967.

T. H. Okabe et al., Materials Transactions, JIM, **44, No. 7 (2003), pp. 1386–1393.

***Y. Kayanuma et al., Journal of Alloys and Compounds, **365** (2004), pp. 211–220.

E-pH diagram

(a) Pt-H₂O system ($a_{\text{Cl}^-} = 0$)



(b) Pt-H₂O-Cl system ($a_{\text{Cl}^-} = 0.48$)

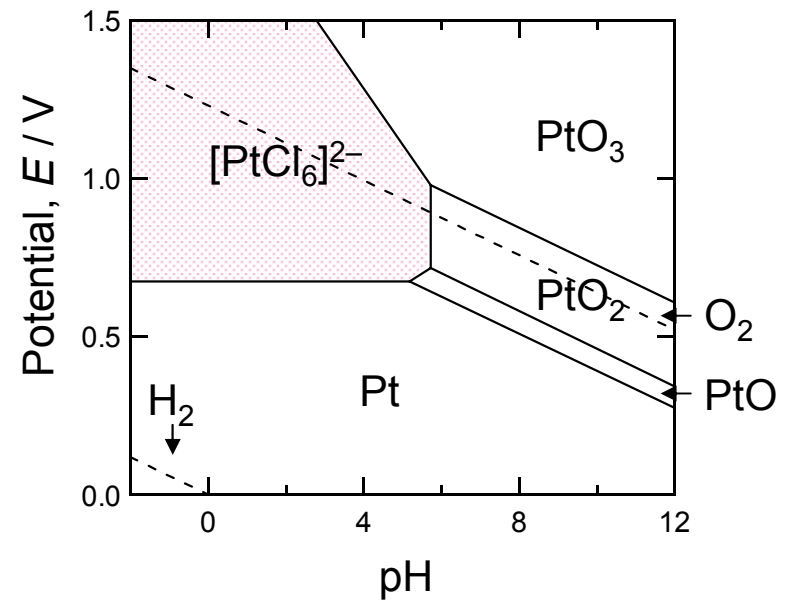


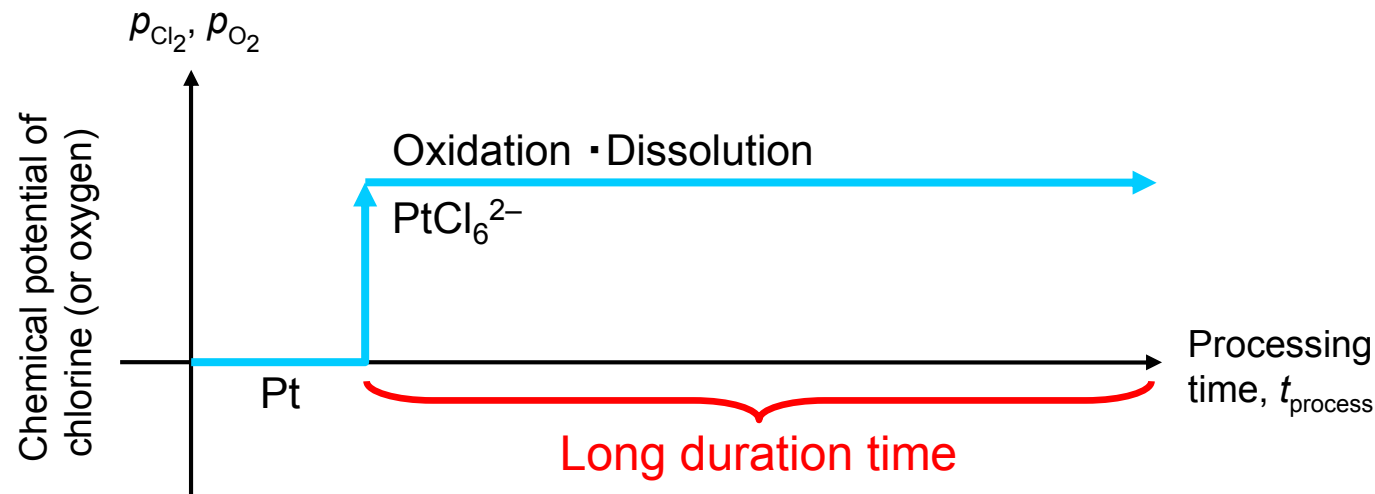
Fig. E-pH diagram of (a) Pt-H₂O and (b) Pt-H₂O-Cl systems at 298 K.

Oxidizing agent is required for the dissolution of precious metals.
 → However, when chloride compound is formed, it is possible to dissolve precious metals in acid without using an oxidant.

Purpose of this study

Development of a new method for dissolving precious metals by reactive metal treatment followed by chlorination

(a) Conventional leaching process



Long processing time and considerable amount of acids with strong oxidants are required for the dissolution.

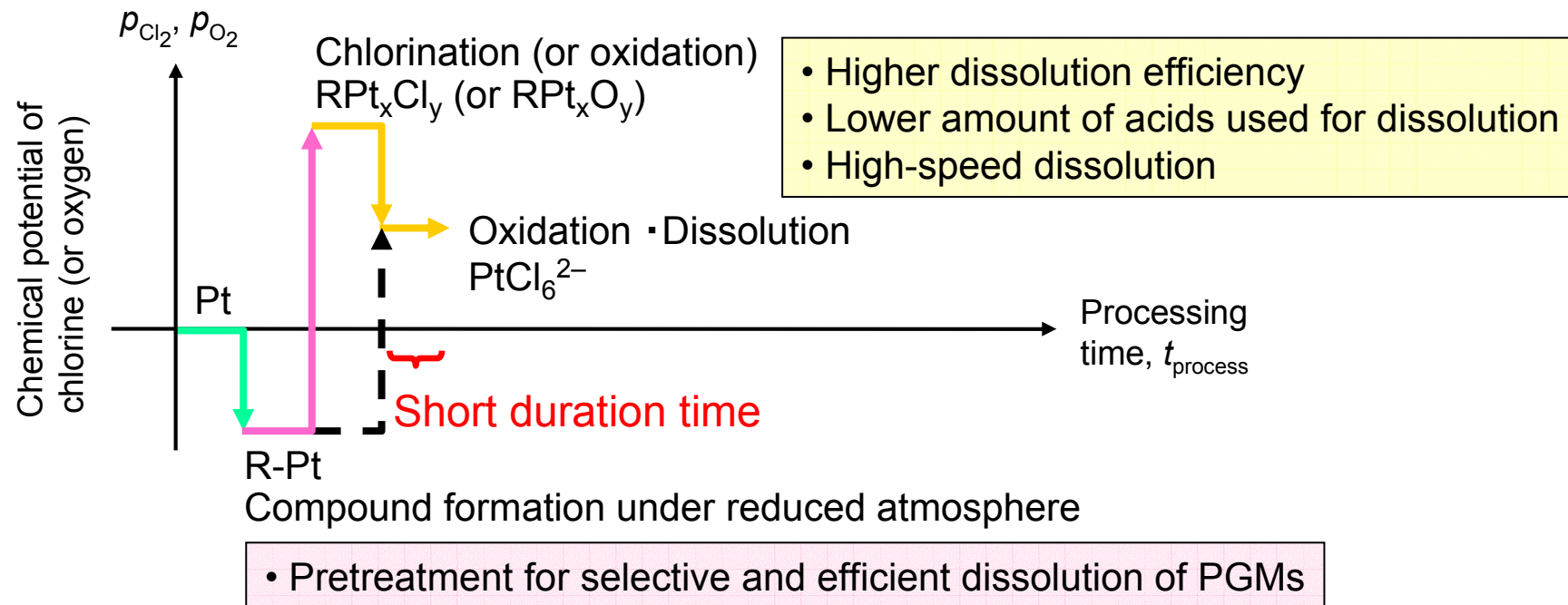


A large amount of waste solution containing heavy metals and strong acids is generated.

Purpose of this study

Development of a new method for dissolving precious metals by reactive metal treatment followed by chlorination

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



Discharge volume of waste solution can be reduced and chloride waste (e.g., $FeCl_3$) can be utilized.

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1. Introduction

2. Experimental

- Flowchart of this study
- Synthesis of Mg-M compounds
- Chlorination of Mg-M compounds

3. Results

4. Summary

Flowchart of this study

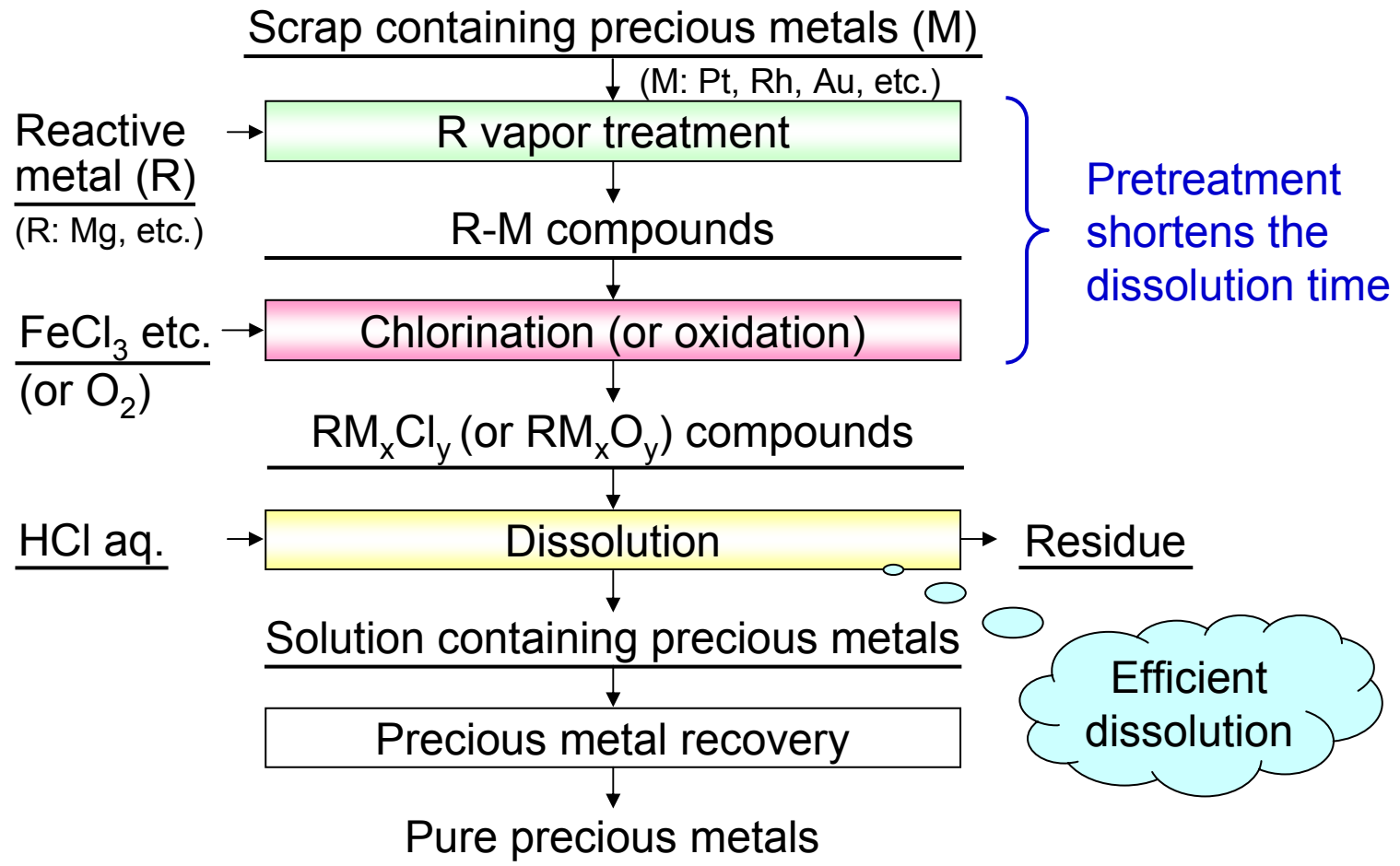
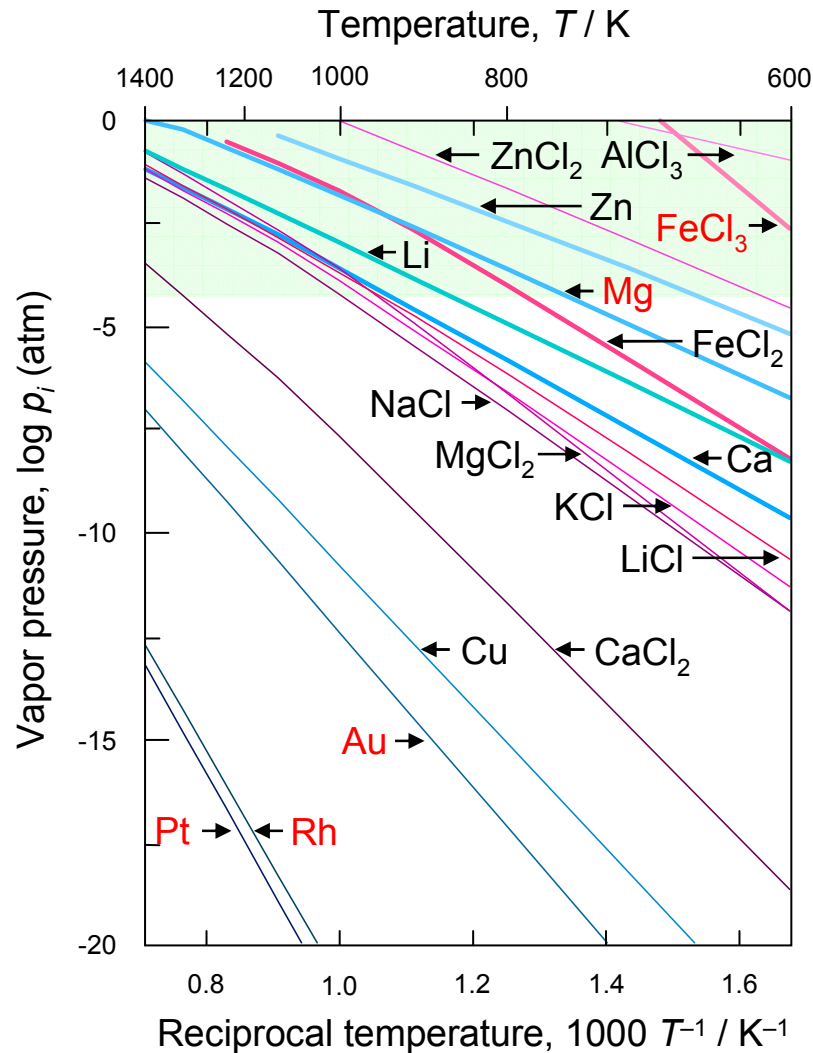


Fig. Precious metal recovery through the formation of complex chlorides (or oxides) by chloride vapor treatment.

Vapor pressure of selected metals and chlorides



Supplying extraction medium
in vapor form

➔ Reactants can be supplied to
the entire quantity of scrap,
irrespective of its complicated
structure.

Fig. Vapor pressure of selected metals
and chlorides as a function of
reciprocal temperature.

Synthesis of Mg-M compounds

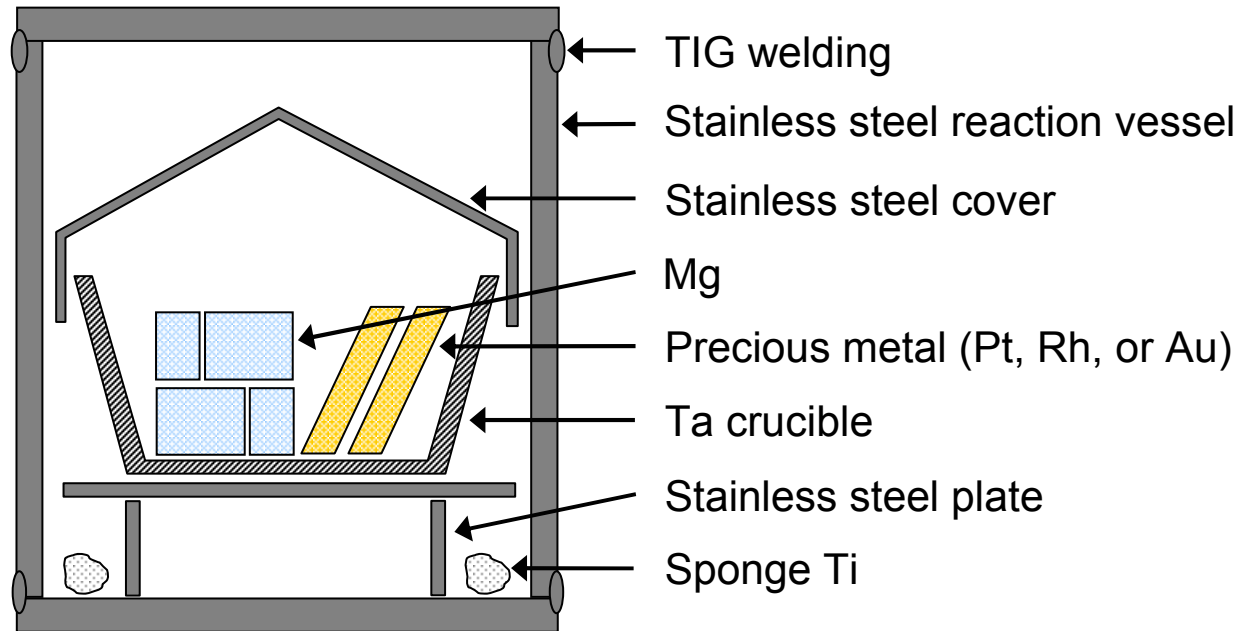


Fig. Schematic illustration of the experimental apparatus for the synthesis of Mg-M compounds.

- Pure precious metals were reacted with molten Mg at 1173 K for 12 h.
 - SEM/EDS analysis: Homogeneous compounds were obtained.
 - XRD analysis: Mg-M compounds were formed (but their phases were not identified).

Chlorination of Mg-M compounds

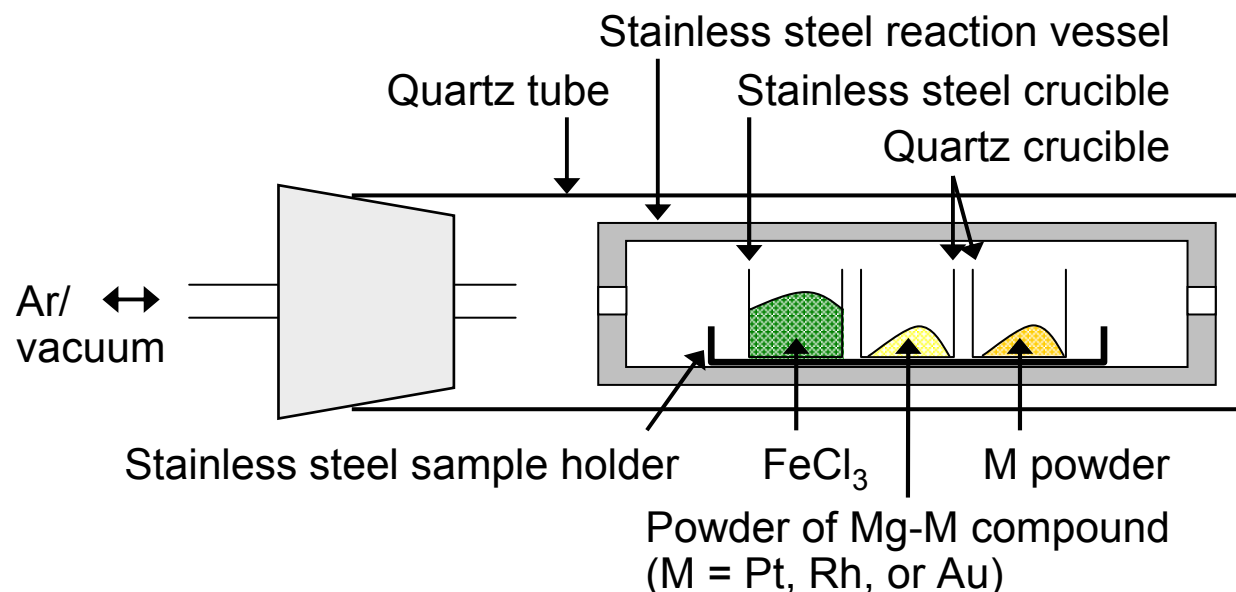
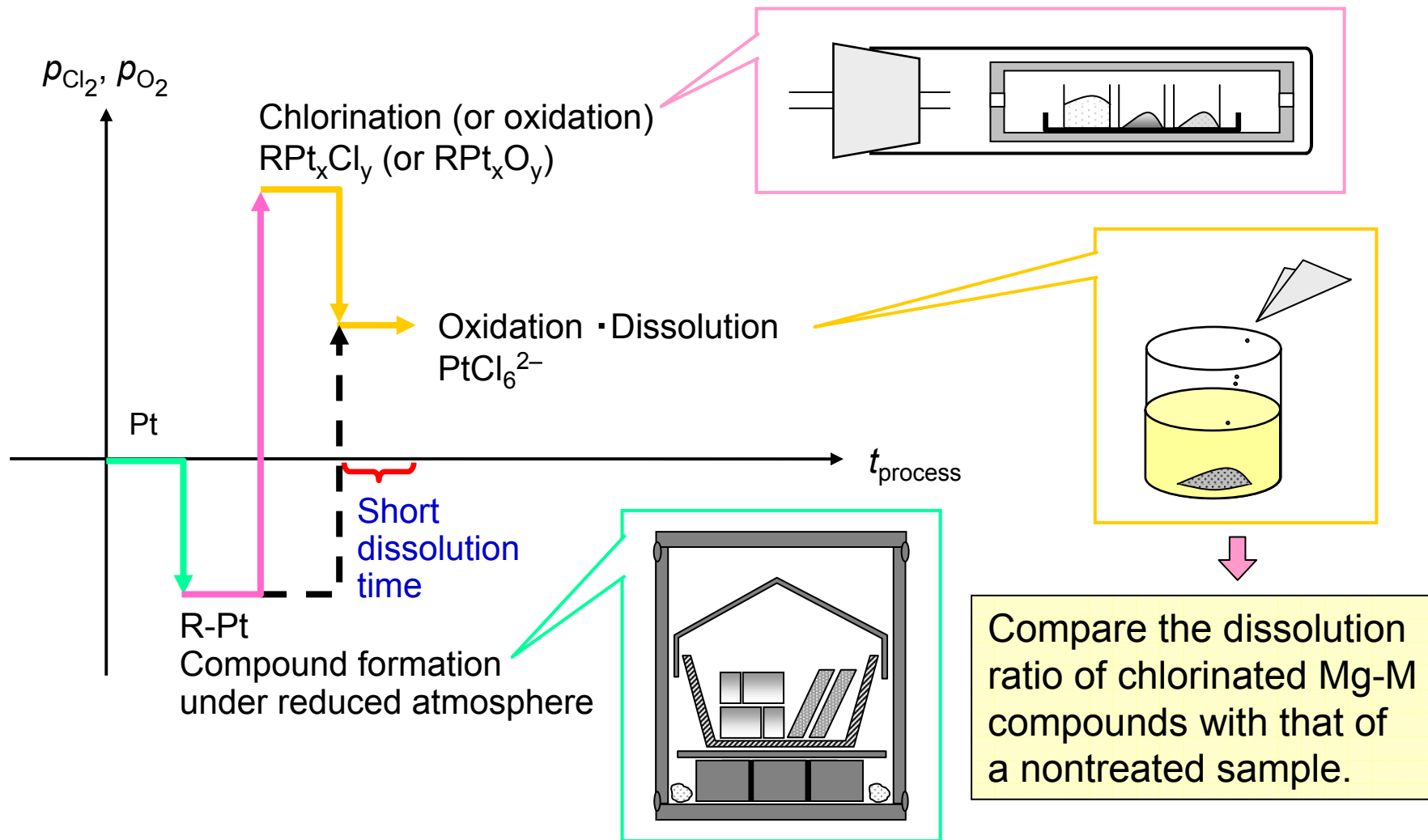


Fig. Schematic illustration of the experimental apparatus for the chlorination of Mg-M compounds.

- Mg-M compounds were reacted with FeCl₃ vapor at 673 K for 3 h.
 - Mass change: The increase in the mass of Mg-M compounds after chlorination was greater than that of pure precious metals.
 - XRD analysis: Identification of the phases in the samples was difficult due to the absence of relevant reference data.

Summary of experimental flowchart



New Extraction Process of Precious Metals from Scrap by Chemical Vapor Treatment

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- 3. Results**
 - Dissolution experiment
 - SEM analysis
4. Summary

Dissolution experiment

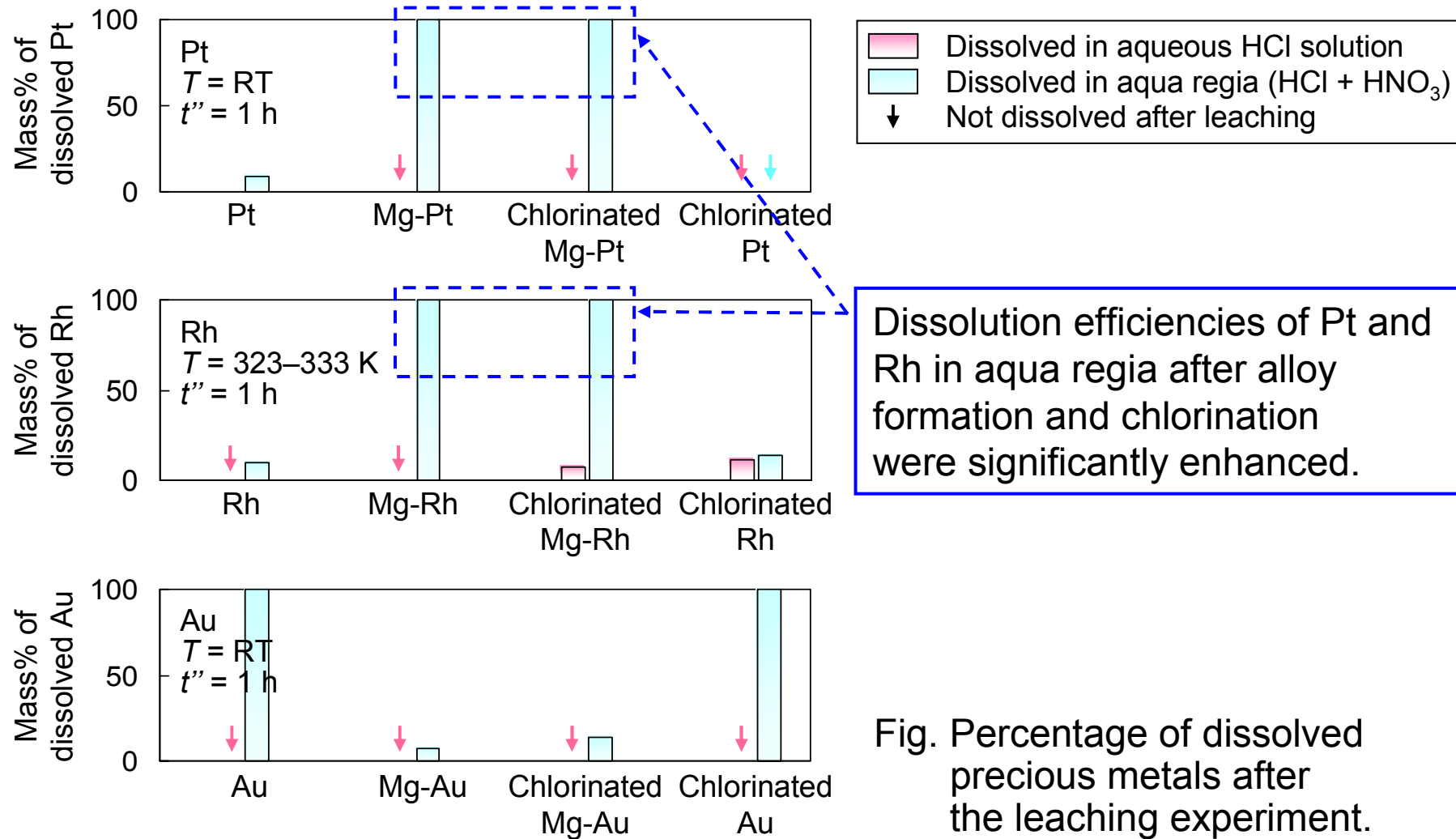


Fig. Percentage of dissolved precious metals after the leaching experiment.

Dissolution experiment

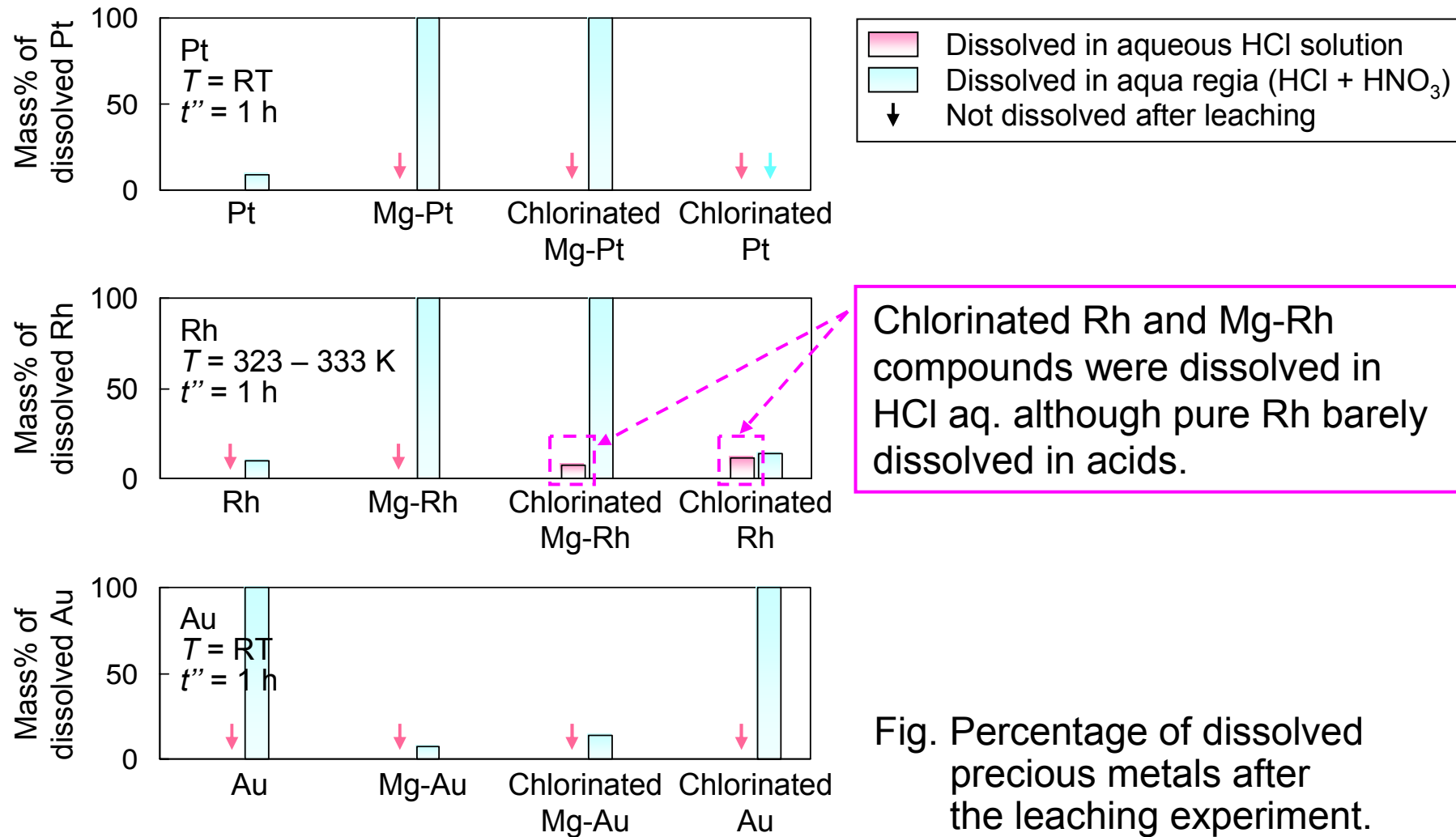


Fig. Percentage of dissolved precious metals after the leaching experiment.

Dissolution experiment

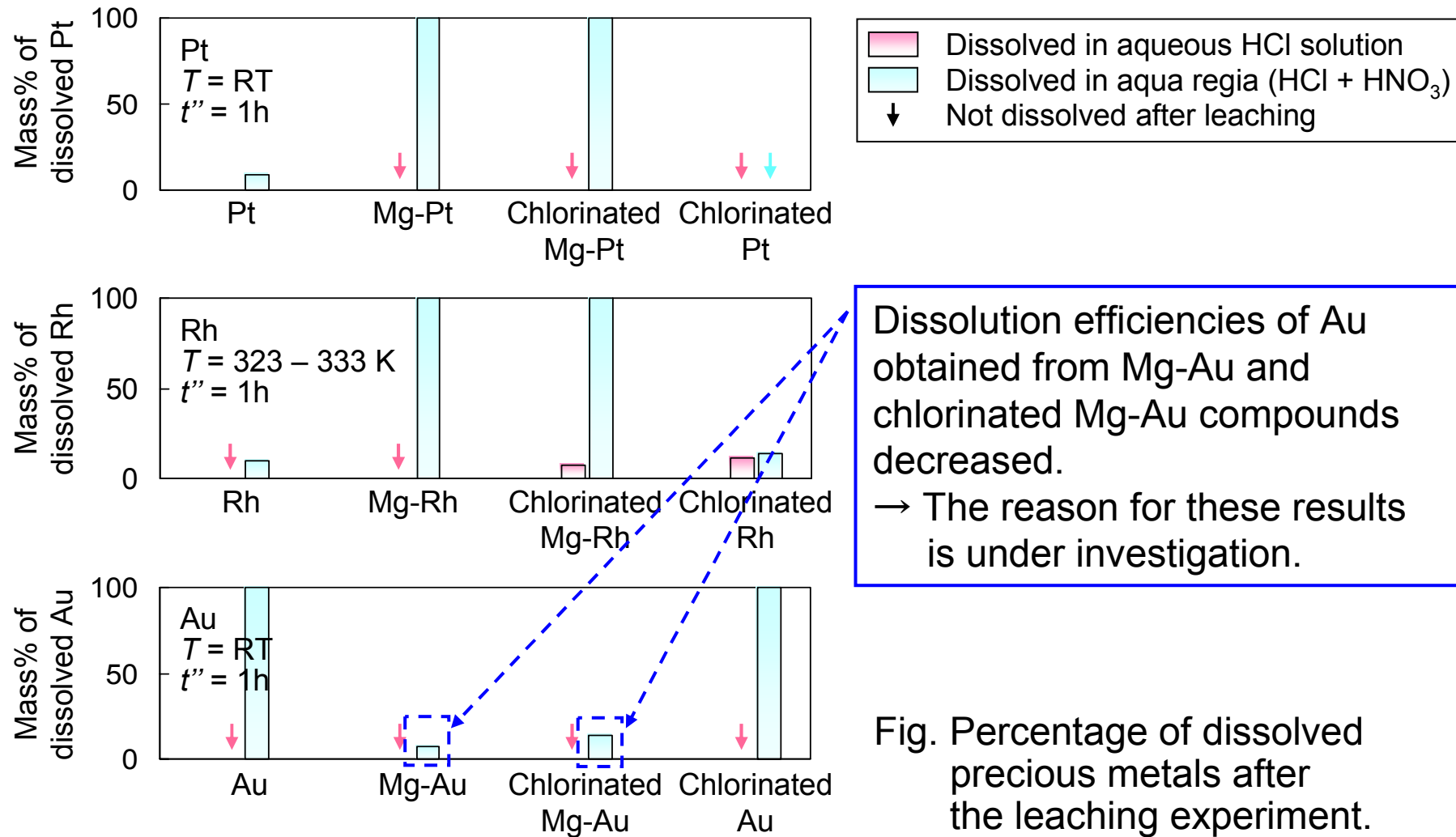
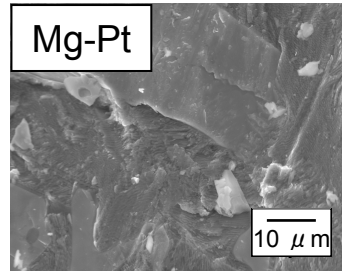


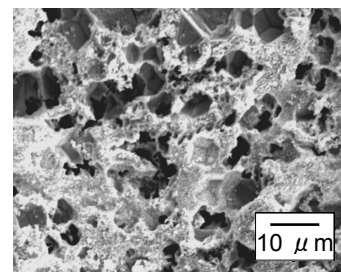
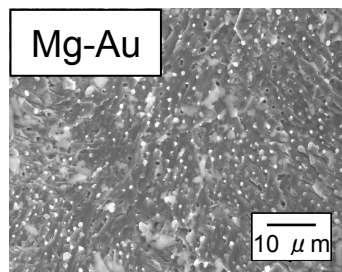
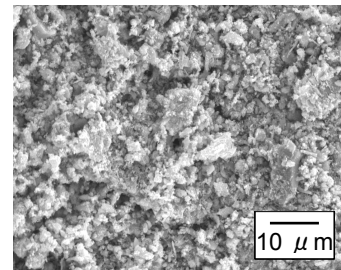
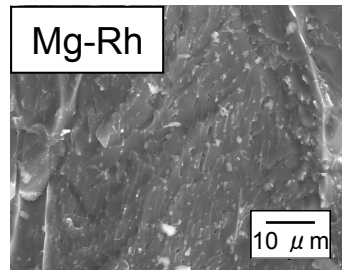
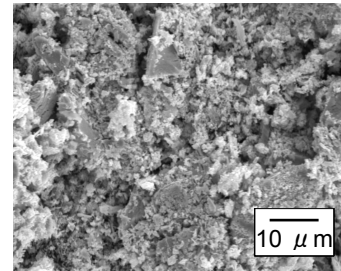
Fig. Percentage of dissolved precious metals after the leaching experiment.

SEM analysis

(a) Before leaching



(b) After HCl aq. leaching

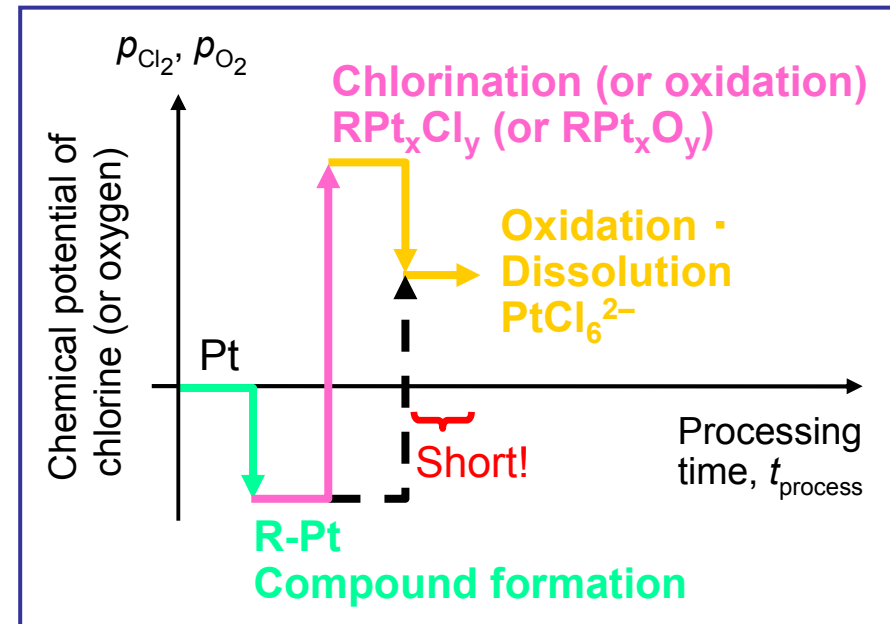


- Mg and Fe were dissolved, and their mass ratios became less than 1 mass% after leaching.
- Grains of precious metals with several microcracks were obtained as residues after leaching in HCl aq.
- Large surface areas of Pt and Rh that formed after/during dissolution of Mg and Fe caused an increase in the dissolution efficiencies of chlorinated Mg-M compounds.

Fig. Scanning electron micrograph of Mg-M compounds before and after leaching with HCl aq.

Summary

1. Reactive metal treatment followed by chlorination was conducted for increasing the dissolution rate of precious metals.
2. Precious metals were reacted with molten Mg at 1173 K for 12 h. The obtained compounds were chlorinated using FeCl_3 vapor at 673 K for 3 h.



3. After the treatments, dissolution efficiencies of Pt and Rh in aqua regia were significantly enhanced. This is probably due to the large surface areas of Pt and Rh formed after/during the preferential dissolution of Mg and Fe. Chlorinated Rh and Mg-Rh compounds were dissolved in HCl aq., although pure Rh was absolutely not dissolved.