Technology for the Recovery of Os and Ru from Primary/Secondary Resources

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Abstract

Some methods used for the recovery of osmium and ruthenium from primary/secondary sources are reviewed. Both Ru and Os could form volatile oxides which enable their separation from the other PGMs by distillation as a traditional method. In hydrochloric acid solution, they also form chloro-complexes with different valence states. Amines or amine based mixture have been used to extract Ru. Solvating extractants are employed to separate Ru and Os. The detailed extraction and stripping conditions of several solvent extraction processes have been reviewed. As an alternative to solvent extraction, solid-liquid method can be applied to recover trace amount of these metals.

Key words: Osmium, ruthenium, solvent extraction, distillation, recovery

1. Introduction

Platinum group metals (PGMs), including Pt, Pd, Rh, Ir, Os and Ru are famous for their wide range of applications, many of which are based on their high melting-points, resistance to corrosion and catalytic properties. ¹ Ruthenium complexes are commonly used in catalysts for metathesis, Fischer-Tropsch, oxidation and hydrogenation reactions. They also play an important role in traditional and nuclear medicine as a potential anti-

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cancer drug and in drug design. Ruthenium is a raw material for the manufacture of various alloys for specific purposes. Osmium and its alloy are used as catalyst in petrochemical processing. In electronic industry, it could be used in electric resistance, electric relay, electrode of spark plug, thermocouple, printed circuit etc. In classic industry, it was used as lining of the reaction container for optical glass manufacture. And Os-Ir alloy are used in making bearing of watch and machines, manufacture of pen tips and stylus.3

The PGMs often occur in nature in the free state but not pure. Platinum and palladium are also found as sulphides in Cu-Ni sulphide deposits. The PGMs are then finally recovered in the anode slimes from the production of electrolytic nickel or copper. Among platinum group metals, Pd and Pt could be dissolved in aqua regia, whereas Rh, Ir, Os, and Ru are relatively inert. Moreover, all PGMs could be dissolved in molten bases such as sodium, phosphorus, silicon, arsenic, antimony and lead.4-5

Unlike other PGMs, both Ru and Os could form volatile oxides which enable their separation from the other PGMs by distillation. Research on the recovery of Ru and Os are limited. Gindin reviewed separation methods of the PGMs based on solvent extraction and ion exchange chromatography which had been developed during 1907-1970.6 The most usual way for recovering ruthenium and osmium from platinum group metals (PGMs) industrial refinery liquors is still by its distillation.6-8 Since PGMs could form chloro-complexes of different valence states, depending on the acid and chloride content of the aqueous phases, and some of them easily change the oxidation states of the metal ion under those conditions. However, numerous research efforts have been made to find a successful separation method.

In this article, the different technologies to recover Os and Ru from primary and secondary sources are reviewed.

2. Recovery of Os and Ru from primary/secondary sources by various methods

2.1. Dissolution of Os and Ru from various materials

The typical compound of Ru and Os and their general physical properties are shown in Table 1.4 In solution, tetravalent compounds of Ru and Os are most stable, and they could be used to make standard solution in laboratory. Besides, Ru(I) and Ru(II) were only found in slow reaction procedure because they are not stable.5

2.1.1. Dissolution of Os and Ru by aqua regia/inverse aqua regia

Yang9 and Pearson10 summarized dissolution methods of Re-Os in the geological samples. Cohen and Waters11 digested Os from geological samples in aqua regia, and the obtained solution was ready for the subsequent purification and measurement of Os. Following the same methodology, Pearson10 used “inverse” aqua regia (5 ml conc. HNO₃, 2 ml conc. HCl) to dissolve their geological sample.

2.1.2. Dissolution of Os and Ru by Na₂O₂ followed by water leaching

Diamantatos12 proposed an integrated scheme for the determination of PGMs and Au from a single lead collector button. The button is parted with perchloric acid and acetic acid after heating at 160-180°C. Iridium and ruthenium and most of Osmium were remained in the residue. Os and Ru was fused with Na₂O₂ and then transferred to solution by leaching with water and Ir was left in the residue.

2.1.3. Dissolution of Os and Ru by KNO₃ and KOH followed by water leaching

The mixture of KNO₃ and KOH was used as an alkali fusion agent to dissolve Ru from spent Ru/ZrO₂ catalyst.13 Temperature increased from room temperature to 650°C, and maintained for 3 hours. Then the reactant mixture was leached by boiled water. Ruthenium was dissolved from the spent catalyst and existed as sodium ruthenium in the leaching solution.

Dissolution of Ru with mixture of KNO₃ and KOH in the procedure of recovery of ruthenium from spent Ru/AI₂O₃ catalyst was also reported.14

The mixture of KNO₃ and KOH was also used in digestion of residue obtained during production of tips of fountain pen.5 The materials contains 5~40% of Ru,
5 ~ 15% of Ir, 0 ~ 2% of Os, < 1% of Pt and Rh, together with small amount of W, Ni, Co, Fe, and SiC.

2.1.4. Dissolution of Os and Ru by leaching with HCl and Cl₂
In the present industry, such as INCO, Matthey Rustenberg, and Lonrho, Ru and Os together with other metals were dissolved by leaching with HCl and Cl₂, and after neutralization /conditioning, osmium and ruthenium were recovered by distillation or anion exchange.¹³⁻¹⁵

2.2. Recovery of Os and Ru from various solutions by distillation
In recovering ruthenium and osmium from different leaching solutions, distillation method was mostly used and modified in many research.

2.2.1. Recovery of Ru from spent catalyst leaching solution
In Zhu and Liu’s research¹³⁻¹⁵ RuO₄ gas was produced during the vacuum distillation at 75 →, with the mixture of NaClO and H₂SO₄ as oxidant. The obtained RuO₄ gas went through a HCl-alcohol solution (1:1), and ruthenium (VIII) was reduced to ruthenium (III). After drying the RuCl₃ solution, β-RuCl₃×H₂O was obtained. In this study, the alkali fusion and oxidation distillation procedure are important and the related reaction were represented as

\[
\text{RuO}_4 + 6\text{KNO}_3 + 2\text{KOH} = \text{K}_2\text{RuO}_3 + 3\text{K}_2\text{O} + \text{H}_2\text{O} + 6\text{NO}_2
\]

(1)

\[
\text{K}_2\text{RuO}_4 + \text{NaClO} + \text{H}_2\text{SO}_4 = \text{NaCl} + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} + \text{RuO}_4
\]

(2)

\[
2\text{RuO}_4 + 16\text{HCl} = 2\text{RuCl}_3 + 8\text{H}_2\text{O} + 5\text{Cl}_2
\]

(3)

This method was used to recover Ru from the spent ruthenium catalyst with (Ru/ZrO₂) and without (Ru) supporter. For both cases, the recovery of Ru was higher than 90% and 93%, respectively. In the research of Liu,¹⁴ the same oxidant agent was employed and the recovery of Ru from Ru/Al₂O₃ spent catalyst reached 93%.

2.2.2. Recovery of Ru and Os from the leaching solution from the residue of pen point manufacture
Zhang¹⁵ reported a procedure to separate and recover Os, Ru and Ir from the residue resulted from the production of tips of fountain pen. RuCl₃ solution was obtained with the same procedure by Zhu and Liu’s research.¹³⁻¹⁵ In the following process, instead of drying the RuCl₃ solution, Ru metal was obtained by first adding ammonia chloride to RuCl₃ solution and then the mixture was roasted and hydrogen gas was purged for the reduction of Ru. In the case of Os, the OsO₄ was absorbed by a mixture of NaOH and alcohol solution. The obtained

<table>
<thead>
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<th>Table 1. The physical properties of Ru and Os.¹⁵</th>
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<tr>
<td>Atomic number</td>
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<tr>
<td>Atomic weight</td>
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<td>Density (g/L)</td>
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<td>Melting point (°C)</td>
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<td>Resistivity (microhm.cm at 20°C)</td>
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osmium sodium salt was reacted with Na₂S and then reduced to Os by hydrogen. The impure Os was processed through oxidation and reduction to get Os with high purity. The general scheme of this procedure is represented as

\[
\begin{align*}
\text{Ru} & \xrightarrow{\Delta} \text{RuCl₃} \xrightarrow{\text{reduce}} \text{RuCl₃} \xrightarrow{\text{HCl} + \text{H₂O}} \text{RuCl₃} \\
\text{Os} & \xrightarrow{\Delta} \text{OsCl₅} \xrightarrow{\text{HCl} + \text{H₂O}} \text{OsCl₆} \xrightarrow{\text{HCl} + \text{H₂O}} \text{OsCl₆} \\
\text{Na₂O⁺} & \xrightarrow{\Delta} \text{OsCl₆} \xrightarrow{\text{HCl} + \text{H₂O}} \text{OsCl₆} \xrightarrow{\text{HCl} + \text{H₂O}} \text{OsCl₆} \\
\end{align*}
\]

and then adsorbed in alkali solution. When the HCl solution has been left for a long time, some Os can be absorbed. Therefore, the OsCl₆ in the HCl solution should be distilled promptly.

2.3. Solvent extraction

2.3.1. Extraction separation of Os and Ru by -N containing extractants

Amines 300 (tri-n-octyl amine) and 336 (Aliphatic quaternary ammonium salt) were employed in the extraction of Ru(III). It has been reported that the extraction behavior of Ru(III) was affected by the concentration of chloride ion. Ru(III) was efficiently extracted from 4 M chloride solutions containing 0.2 M hydrogen ion, but the stripping of Ru(III) from the loaded amine was difficult. The stripping agent was NaCl and a mixture of NaOH and NaCl solution for Alamines 300 and 336, respectively. In the case of Aliquat 336, a mixture of NH₃ and NHCl or NaHCO₃ was used. An anion exchange mechanism was proposed for the extraction of Ru(III) with amines from chloride solutions.

When LIX 54 (a β-diketone) was added to Alamine 336 or Aliquat 336, the extraction and stripping behavior of Ru(III) was improved with the use of this mixture. Moreover, it was possible to separate Ru(III) from the mixed solution of Rh(III) and Ir(IV) by extraction with this mixture. A cation-exchange mechanism was suggested for the extraction of Ru by the mixture. The higher stripping percentage of Ru (III) may be ascribed to the re-protonation of LIX 54.

Besides, a mixture of Alamine 336 and TBP was developed to separate Ru(III) from Rh(III) and Ir(IV). In extraction of Ru from the mixed solution containing Ir and Rh with the mixture of Alamine 336 and TBP, Ir(IV) was first extracted and then Ru(III), leaving Rh(III) in the raffinate.

P. Malik and A. P. Paiva investigated the extraction of Ru(III)/ Ru(IV) from hydrochloric acid solution with DMDCHMA (N, N’-Dimethyl- N, N’- Dicyclohexyl(malonamide) dissolved in 1,2-dichloroethane. According to their research results, the extraction behaviors of Ru(III)/ Ru(IV) depended on the concentration of HCl in the aqueous
solution. When the concentration of HCl was in the range of 5 to 7 M, the extraction percentage of Ru(III)/Ru(IV) was similar to each other. In their work, the extracted species of Ru(III) and Ru(IV) was discussed and compared with other extractants, such as Alamine 336, Cyanex 923, and dihexyl sulfosilicate.\textsuperscript{18-22} They concluded that [RuCl\textsubscript{3}^2-\textsuperscript{2H}^3\textsuperscript{3L}] and [RuCl\textsubscript{2}^2-\textsuperscript{2H}^3\textsuperscript{3L}] were the extracted species of Ru(III) and Ru(IV), respectively, where L represents DMDCHMA.

Besides individual metal solution, extraction of the other PGMs and associated elements were also investigated. From the synthetic solution containing Pt, Pd, Rh, Ir, and Ru, only Ru and Pd can be selectively separated by extraction with DMDCHMA and then the loaded Ru and Pd were stripped with water. Rh(III) was not extracted, and the extraction of Pt and Ir was not possible due to the formation of a third phase. In another context, DMDCHMA was found to be unsuitable to separate Ru from the other associated metal ions, such as In (III), Co (II), Cu (II), Fe (III), Mn (II), Zn (II) except Ni (II).

Trioctylamine has also been included in an emulsion liquid membrane to concentrate Ru from lean HCl solutions, tin (II) chloride being employed to enhance ruthenium extraction.\textsuperscript{23}

2.3.2. Extraction separation of Os and Ru by −P containing extractants

Cyanex 925 (a liquid mixture containing 19 components with 26.4% tri(2,4,4-trimethyl pentyl) phosphine oxide and tri-octyl phosphine oxide (65.9%))\textsuperscript{24} was employed as an extractant to separate Os(VIII), Ir(IV), and Ru(III) from aqueous chloride media in the absence and presence of tin(II) chloride. From HCl solution in the absence of tin(II) chloride, Os and Ru were extracted quantitatively, while the extraction of Ir was incomplete. Besides, Os (VIII) could be extracted at lower concentrations (0.01-0.05 M), while Ru(III) at higher concentrations (3.5-5.0 M).

In the presence of tin (II) chloride, Ir (III) was reduced to form Ir(I)-tin complexes which were more extractable. In the same condition, Ru (IV) was reduced to less-extractable Ru (III), and Os was also reduced to a less-stable oxidation state lower than the tetravalent. In the presence of tin(II) chloride, the extracted species of Os(VIII) and Ru(IV) might be OsCl\textsubscript{4}-Cyanex 925 and RuCl\textsubscript{2}-Cyanex 925, respectively, Ir was extracted as [Ir(HCl\textsubscript{2})\textsubscript{3}]\textsuperscript{3-}\textsuperscript{2H}^3\textsuperscript{cy} Cyanex 925.

A process was developed to separate these three metal ions by using Cyanex 925. Os was first extracted at lower HCl concentration (0.025 M) and SnCl\textsubscript{2} was added to the raffinate which contains Ru and Ir. After adjusting the concentration of HCl to 1.0 M, Ir was extracted by Cyanex 925, leaving Ru in the raffinate. The loaded Os and Ir in Cyanex 925 was stripped by 2.0 M thiourea and 8.0 M HCl, respectively. The recovery percentage of Os and Ru was 99.4% and 98.8%, respectively. The general flow-sheet is shown in Fig. 1. This method was applied to recover these metals from organometallic catalyst.
Additionally, Cyanex 921 (tri-octyl phosphine oxide)\textsuperscript{25} was used in solvent extraction separation of osmium, ruthenium, and iridium. In this literature, the extraction behavior of Ru and Os with Cyanex 921 was found to depend on the concentration of HCl and similar to that of Cyanex 925. The Os loaded in Cyanex 921 was stripped by 2.0 M thiourea and the recovery of Os was 99.42\%. By adding tin(II) chloride, Ir was separated from Ru by extraction with Cyanex 921, leaving Ru in the raffinate. The loaded Ir was recovered by stripping with 6.0 M HNO\textsubscript{3} and the recovery of Ru was 98.89\%.

Separation of Os, Ru and Ir in chloride acid solution was exploited by taking advantage of the differences in their extraction and stripping behaviour by Cyanex 923.\textsuperscript{30} Os was extracted by 0.1 M Cyanex 923 when the concentration of HCl was 0.025 M and was recovered by stripping with 1.0 M thiourea. Ir and Ru was separated by co-extraction after adjusting the concentration of HCl to 7 M, and selectively stripping by 4.0 M HNO\textsubscript{3} and 1\% ascorbic acid in 1.0 M HCl.

2.3.3. Extraction separation of Os and Ru by –Carbon containing compound

Meadows and Marlack,\textsuperscript{26} and Morgan\textsuperscript{27} investigated the possibility of extracting Os and Ru from acidic solutions using organic solvents, and this method was first applied to geological analysis by Crockett et al.\textsuperscript{28}

Cohen and Waters\textsuperscript{11} partitioned OsO\textsubscript{4} directly from the aqua regia digest solution into an organic phase, either CCl\textsubscript{4} or HCCl\textsubscript{3}, and then Os was recovered by back extraction into concentrated HBr. Following a simple micro-distillation step, the purified sample was ready for thermal ionization mass spectrometry (TIMS). Similarly, in another research,\textsuperscript{10} extraction of Os by CCl\textsubscript{4} was employed from geological samples digested in inverse aqua regia, and then Os was stripped by 9N HBr. After drying HBr solution, the concentration of Os was measured by ICP-MS.

Finally, Ru(III) extraction from HCl solutions has also been studied using bisacylated triethylenetetramine,\textsuperscript{29} and dibenzy sulfoxide,\textsuperscript{30} neutral diamide compounds,\textsuperscript{31} 4-pyridone derivatives\textsuperscript{32} and N-octylamine\textsuperscript{33} (for Ru(IV)).

![Fig. 2. The separation of various metals by using DOAA at different acid concentration.\textsuperscript{29}]

2.4. Reversed-phase paper chromatography

Some authors have tried to separate Ru and Os ions by employing reversed paper chromatography with various agents, such as DOAA (N,N-di-sec-octylacetamide) (in benzene),\textsuperscript{34} DEHSO (Di-2-ethylhexyl) sulfoxide) (in dodecylbenzene),\textsuperscript{35} S-carbamimidohio acid phenylmethylster monohydrochloride, and S-hexadecyl thiourea hydrochloride (in alcohol).\textsuperscript{36} The relation of reversed phase paper chromatography and liquid-liquid extraction was studied in literature.\textsuperscript{29} In these papers, the extraction behavior of metal ions in the related system was investigated by varying the concentration of mobile phase. And their R\textsubscript{f} graphs were drawn against the concentration of HCl, from which the possibility of separation of certain metal ions could be estimated. The separation behavior of metals by DOAA was illustrated in Fig. 2.

2.5. Other Solid-liquid approach

A trace level concentration of Os (VIII) was quantitatively extracted from 1 M HCl with N-octylamine as a stationary phase on silica gel.\textsuperscript{37} Compared with solvent extraction method using N-n-octylamine,\textsuperscript{38} some drawbacks such as interferences from anions and cations were avoided. Silica, which was chemically modified with a thiourea derivative bearing a triphenylphosphonium chloride group,\textsuperscript{39}
was used on the sorption of osmium and ruthenium in different oxidation states. The use of activated carbon pellets to selectively separate Pd(II), Ru(III), and Rh(III) was also reported. All these liquid-solid works deserve mention.  

3. Conclusions

The most promising techniques for recovery of Os and Ru from primary/sub- secondary materials were reviewed in this study. Although some of these researches were carried out at laboratory scale and good results were obtained, there are some limitations for practical application of these results. Traditionally, pure Os and Ru with purity higher than 99% was obtained by distillation from the leaching solution but the processes are complex. Compared with traditional distillation method, solvent extraction and liquid-solid phase methods have the advantage of producing pure Os and Ru metal in fewer steps. In solvent extraction, amines or a mixture of amine with solvating extractants have been employed to extract Ru from the leaching solution. Recovery of Ru by amines suffered from low stripping efficiency, but this drawback was overcome by adding LIX54 to amine. Solvating extractants have been tried to separate Ru and Os from the leaching solution. Detailed conditions for extraction and stripping have been investigated. The advantage of using N-octylamine as a stationary phase on silica gel over solvent extraction indicated the importance of solid-liquid method in future development. Therefore, finding extractants and resins/other solid phase with cheap price, high selectivity and loading capacity for recovery of osmium and ruthenium is the important task for refining researchers.

감사의 글

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  V: 동권 제41호~제50호, VI: 동권 제51호~제62호, VII: 동권 제63호~제74호, VIII: 동권 제75호~제86호.

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