/
Article / Book Information

( )	-
Title(English)	Development of Rapid and Efficient Extraction for Inert Platinum Group Metals by Designing Inner Sphere Coordination and Outer Sphere Interactions
( )	ZhengZhiwei
Author(English)	Zhiwei Zheng
( )	: ( ), : , : 12233 , :2022 9 22 , : , : , , , ,
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number: 12233 , Conferred date:2022/9/22, Degree Type:Course doctor, Examiner:,,,,
( )	
Category(English)	Doctoral Thesis
( )	
Type(English)	Outline

Thesis Title: Development of Rapid and Efficient Extraction for Inert Platinum Group Metals by Designing Inner Sphere Coordination and Outer Sphere Interactions

High level radioactive waste (HLW) always contains several platinum group metals (PGMs) like Pd, Rh, and Ru. Separation of them is highly required, because they cause the serious problems in vitrification of HLW and have some isotopes showing long-lasting radioactivity. Additionally, high demands and limited availability of PGMs are concerned recently. It is highly relevant to recover and recycle PGMs from wasted materials like electronic devices and automotive catalysts. Solvent extraction is a promising method for the separation and recovery of PGMs, while extraction of some PGMs like Ru(III) and Rh(III) always shows slow kinetics and low efficiency. This doctoral thesis successfully solved these issues and demonstrated how to rapidly and efficiently extract inert PGMs from practical aqueous systems like HNO_3(aq) and HCl(aq)

This doctoral thesis consists of 6 chapters. Each chapter is described as follows.

Chapter 1. Introduction

This chapter introduced two backgrounds for this study including the serious problems in the nuclear fuel cycle caused by PGMs and issues about high demands and limited availability of PGMs. Based on these backgrounds, development of separation and recovery of PGMs is necessary. However, solvent extraction as a promising method always shows slow kinetics and low efficiency for some PGMs like Ru(III) and Rh(III) because of their internees. Although the previous studies reported that the thermal-assisted technique including microwave and convection heating can accelerate the extraction of these inert PGMs, these studies always use an ionic liquid as organic solvent and extractant. Ionic liquids are still difficult to use in actual extraction because of their high cost and inability to change extractants. Therefore, the objective of this doctoral thesis is to clarify whether the thermal-assisted technique is also suitable for the extraction of inert PGMs in ordinary organic solvent systems. Furthermore, I also intend to establish and demonstrate a realistic PGMs extraction method with thermal assistance for the accelerated extraction of inert PGMs.

Chapter 2. Thermal-Assisted Solvent Extraction in Ordinary Organic Solvent System

This chapter is to expand the thermal-assisted technique from limited ionic liquid systems to ordinary organic solvent systems. I studied the thermal-assisted extraction behaviors of Ru(III) and Rh(III) from 0.5 M HNO(aq) to a selected ordinary organic solvent such as 1-octanol system, where a pyridinediamide named TBPDA was employed as a potential ligand. In this ordinary organic solvent system, the extraction kinetics of these inert PGMs indeed was accelerated with thermal-assistance, while the extractability (*E*%) of Ru(III) and Rh(III) was only 29% and 8%, respectively. After comparing the extraction behavior with the ionic liquid

system, I found that extra bis(trifluoromethylsulfonyl)amide Tf$_2$N$^-$, a hydrophobic anion, can improve the E% of Ru(III) and Rh(III) to 95% and 90%, respectively. The extractable species were concluded to be [Ru(NO)(TBPDA)](NO$_3$)$_2$(Tf$_2$N) and [Rh(TBPDA)$_3$](NO$_3$)$_2$(Tf$_2$N), where Tf$_2$N$^-$ as anionic phase transfer catalyst (PTC) is coupled with an extracted species to form a more lipophilic ion pair to be extracted. In this chapter, I successfully confirmed ordinary organic solvents system is also suited for thermal-assisted extraction of inert PGMs

Chapter 3. Complexation-Distribution Separated Solvent Extraction Process in HNO$_3$(aq) System.

The thermal-assisted extraction of inert PGMs has been confirmed in HNO(aq)/ 1-octanol system. To carry out this extraction method, I have to mix and heat aqueous and organic phases together. This heating treatment involves concerns about the difficulty of temperature control in actual extraction contactors and safety risks arising from heating organic solvents.

In this chapter, I established and demonstrated a realistic process named complexation-distribution separated extraction process for inert PGMs. This method consists of two steps, complexation and distribution processes. In the complexation process, I confirmed the water-soluble [M(PDA)]$^{3+}$ complexes (M = Ru(NO), Rh) can be successfully formed in 0.5 M HNO$_3$(aq) under heating treatment. In the next distribution process step, the [M(PDA)]$^{3+}$ complexes in the aqueous phase were rapidly and efficiently extracted to 1-octanol layer at RT within 5 min. The actual forms of extractable species would be [M(PDA)](NO$_3$)$_2$(Tf$_2$N) (M = Ru(NO), Rh), where Tf$_2$N$^-$ significantly enhances the solvent extraction as an anionic PTC. This extraction process proposed in this chapter overcomes the problems caused by thermal-assisted technique in solvent extraction of inert PGMs.

Chapter 4. Complexation-Distribution Separated Solvent Extraction Process in HCl(aq) System

HCl(aq) is more practical aqueous system for precious metals recycling from their social stocks so-called *urban mining*. Inert PGMs have the tendency to form stable anionic chlorocomplexes in this HCl(aq) like [RuCl$_x$]$^{(x-3)-}$ and [RhCl$_y$]$^{(y-3)-}$ (x = 3-6, y = 4-6). To complete the complexation of these PGMs with extractant, the heating time should be sufficiently long. However, the potential ligands, PDA, were hydrolyzed under long contact with acid solution. Thus, I selected other chemically stable ligands such as picolinic acids (Hpic, 3-HMepic) and bipyridines (bpy, 4-DMbpy) towards hydrolysis for extraction of inert PGMs in HCl(aq).

In this chapter, I confirmed that the water-soluble [Ru(L$_1$)$_3$], [Rh(L$_1$)$_2$Cl$_2$]$^-$ and [Rh(L$_2$)$_n$]$^{3+}$ (L$_1$ = pic, 3-Mepic; L$_2$ = bpy and 4-DMbpy) complexes can be formed in 0.5 M HCl(aq) under thermal-assistance. The [Ru(3-HMepic)$_3$] and [Rh(4-DMbpy)$_n$]$^{3+}$ complexes in the aqueous phase were rapidly and efficiently extracted to 1-octanol layer at RT within 5 min, where E% of Ru(III) and Rh(III) reached up to 79% employing 3-HMepic and 4-DMbpy, respectively. The actual forms of extractable species would be [Ru(3-HMepic)$_3$] and [Rh(4-DMbpy)$_n$](Tf$_2$N)(Cl)$_2$, where Tf$_2$N$^-$ significantly enhances the solvent extraction as a salting-

out agent or a cationic PTC. These results suggest that the complexation-distribution separated extraction process is also suitable for the extraction of inert PGMs from HCl(aq). Furthermore, I found Ru(III) can be efficiently separated from Rh(III) employing 3-HMepic because of their different structure of complexes formed in HCl(aq).

Chapter 5. Process Flows and Demonstrations for Separation and Recovery of PGMs

Since chapters 3 and 4 confirmed efficient and rapid extraction of inert PGMs in HNO(aq) and HCl(aq) systems, this chapter proposed and demonstrated process flows for separation and recovery of PGMs from these two aqueous solutions.

HNO_3(aq) is a practical aqueous system for the separation of PGMs such as Pd(II), Ru(III) and Rh(III) from HLW. In the proposed process flow, Ru(III) and Rh(III) were successfully extracted from HNO_3(aq) by DEDPPDA as a ligand and Tf_2N^- as an anionic PTC under a multistage process. After 4 extraction cycle, E% of Ru(III) and Rh(III) was more than 90%. In addition, Pd(II) also has a high potential to be extracted under this method.

HCl(aq) is a practical aqueous system for separation and recovery of PGMs such as Pd(II), Pt(IV), Ru(III) and Rh(III) from *urban mining*. The process flow was proposed to selectively separate these PGMs from their mixture. Herein, I employed a tetrahexylammonium chloride (THACl) to extract Pd(II) and Pt(IV) as step 1, Ru(III) was then separated by 3-HMepic as a ligand and Tf_2N^- as a salting-out agent as the step 2. In step 3, Rh(III) was extracted by bpy as ligand and Tf_2N^- as an anionic PTC. In this process flow, the thermal-assisted technique and complexation-distribution separated extraction process are necessary for the extraction of inert PGMs such as Ru(III) and Rh(III), while the normal solvent extraction is enough for the extraction of Pd(II) and Pt(IV).

Chapter 6. Conclusion

In this chapter, the results from each chapter of the doctoral thesis are summarized.