AN INVESTIGATION ON THE SOLVENT EXTRACTION OF RHODIUM FROM AQUEOUS CHLORIDE SOLUTIONS

**

Elyse Benguerel

Department of Mining and Metallurgical Engineering McGill University Montreal, Canada

September 1991

A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of Master of Engineering

(c) E. Benguerel, 1991.

Solvent Extraction of Rhodium from Aqueous Chloride Solutions

•

For my family...

J.

.

and in memory of the 14 victims of the Ecole Polytechnique massacre (December 6, 1989).

ABSTRACT

ĩ

ź

The aqueous behaviour of rhodium (III) (Rh) in chloride solutions was investigated with the objective of evaluating its response to solvent extraction with 8-hydroxyquinoline derivatives. A theoretical analysis of the abundance of the various chloro-complexes in solution revealed that monoaquopentachlororhodate and hexachlororhodate are the most common forms of Rh(III) in chloride solutions (>0.5M Cl⁻) and that the relative abundance of hexachlororhodate may be lower than was previously reported.

The extraction degree of Rh (III) with 8-hydroxyquinoline derivatives from solutions ranging in acidity from 0.7 to 8.0M and in chloride concentration from 0.7 to 4M was found to follow the calculated abundance of hexachlororhodate (about 5 to 40% in the region investigated). Also, the extraction mechanism was deduced to be ion-pair formation.

The extraction degree of Rh(III) from similar solutions but previously treated with $SnCl_2$, was also investigated, and in this case the extraction was quantitative throughout the acidity and chloride concentration ranges tested. Virtual quantitative stripping can be achieved with four five-minute contacts with 1.7M H₂SO₄ + 1M Na₂SO₄. A preliminary flowsheet for the industrial application of this solvent extraction process for Rh is presented.

iii

<u>RÉSUMÉ</u>

Le comportement du rhodium (III) (Rh) en solution de chlorure a été examiné afin d'évaluer la possibilité d'extraction du Rh(III) par solvant avec des dérivés du 8-hydroxyquinoline. Une analyze théorique de la quantité de divers complexes chlorés du Rh(III) a révélé que $RhCl_5(H_2O)^{2}$ et $RhCl_6^{3}$ sont les deux formes les plus communes du Rh en solution de chlorure (>0.5M Cl⁻) et il est probable que la quantité relative de RhCl₆³ est plus faible que rapportée antérieurement.

On a observé que le niveau d'extraction du Rh en solution acide, dont l'acidité et la concentration totale de chlorure varient respectivement de 0.7 $\stackrel{>}{\sim}$ 8.0M et de 0.7 à 4.0M, à l'aide des dérivées du 8-hydroxyquinoline est proche de la quantité de RhCl₆³ calculée (environ 5 à 40%). Il a aussi été déduit que l'extraction se fait par la formation de paires d'ions.

Le niveau d'extraction du Rh(III) en solutions de chlorure semblables à celles décrites ci-dessus mais traitées avec du SnCl₂ a aussi été étudié, et dans ce cas, l'extraction peut être considérée comme quantitative pour les différentes solutions examinées. D'autre part, la reéxtraction du Rh peut être réalisée avec quatre contacts de cinq minutes de 1.7M H_2SO_4 + 1M Na₂SO₄. En dernière partie, un schéma préliminaire d'un procédé d'extraction par solvant du Rh est présenté pour une application industrielle.

iv

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and appreciation to Professor G.P. Demopoulos for his inspiring supervision, and his continual interest and encouragement throughout the course of this work.

I also especially wish to thank my fellow laboratory colleagues, D. Filippou and V. Aprahamian, for making the work days so pleasant and also for all of their help and assistance both in the laboratory and through insightful discussions.

I would also like to thank all of the members of the Hydrometallurgy research group of McGill University for the their helpfulness and team-like disposition. My fellow office associates, and particularly Ms. L. Gavoret, are also acknowledged for their invaluable help in alleviating the tensions of research work.

Finally, I am also indebted to Noranda Minerals Inc. for their interest and generous financial support during the course of this research work.

TABLE OF CONTENTS

ABS	TRACI		iii		
RÉSUMÉ					
ACK	ACKNOWLEDGEMENTS				
TAB	LE OF	CONTENTS	vi		
LIS	T OF	FIGURES	ix		
LIS	T OF	TABLES	xii		
1.	INTE	RODUCTION	1		
2.	LITE	RATURE REVIEW AND THEORY	3		
	2.1	PGM REFINING PRACTICES	3		
		2.1.1 Rh Recovery	3		
	2.2	THE AQUEOUS CHLORIDE CHEMISTRY OF RHODIUM(III)	7		
		2.2.1 Basic Inorganic Characteristics	7		
		2.2.2 Rh Species in Chloride Solutions	8		
		2.2.3 Speciation	9		
		2.2.4 Rh in Sulfate Solutions	10		
		2.2.5 Rh Chloride Complexes and SnCl ₂	11		
	2.3	SOLVENT EXTRACTION	14		
		2.3.1 Solvent Extraction	14		
		2.3.2 Solvent Extraction with Amines	15		
		2.3.3 Summary of Other Solvent	17		
		Extraction Studies			
		2.3.4 Ion Exchange	21		
3.	SPEC	IATION ANALYSIS AND DETERMINATION	24		
	3.1	Speciation Diagrams	24		
	3.2	Kinetics of Aquation/Anation	32		
4.	EXPE	RIMENTAL PROCEDURE	39		
	4.1	Reagents	39		
	4.2	Rh-Sn Feed Pretreatment	42		
	4.3	Procedure	42		
	4.4	Rh Concentration Determination	43		

RESULTS AND DISCUSSION 5

Í

RESUI	LTS AND	DISCUSSION	44
5.1	Rh EX	TRACTION SUPPRESSION IN AN 8-HYDROXY-	44
	QUINO	LINE Pt/Pd SOLVENT EXTRACTION CIRCUIT	
	5.1.1	Effect of Feed Acidity in the	47
		High Acid Region (0.7 to 8M HCl)	
	5.1.2	Reproducibility of Results	50
	5.1.3	Effect of Contact Time	51
	5.1.4	Effect of Addition of Cl Salt in the	52
		Region 0.7 to 2.7M HCl	
	5.1.5	Rh Extraction in the Low Acid	54
		Region ($pH = 0.5 to 3.5$)	
	5.1.6	Effect of Aging	59
	5.1.7	Effect of the Presence of Sulfate	62
	5.1.8	Stripping Tests	65
	5.1.9	Suppression of Rh in the Pt/Pd	65
		Solvent Extraction Circuit	
5.2	RHODIU	IM EXTRACTION IN MODIFIED	68
	8-HYDR	OXYQUINOLINE SYSTEMS	
	5.2 1	Synergistic 8-Hydroxyguinoline	68
		System for Rh(III)	
	5.2.2	Extraction of Rh(III) by Intermittent	71
		Reequilibration of Aqueous Feed	
5.3	RHODIU	M EXTRACTION IN THE Rh-Sn-Cl/	74
	8-HYDR	CXYQUINOLINE SYSTEM	
	5.3.1	Effect of Feed Acidity in the	74
		Region 0.7 to 8M HCl	
	5.3.2	Sn Co-Extraction	77
	5.3.3	Stripping of Rh from Loaded 8-	78
		Hydroxyquinoline	
	5.3.4	Stripping of Sn from Loaded 8-	83
		Hydroxyquinoline	
	5.3.5	Effect of Recycled Organic on	86
		Loading and Stripping	

		5.3.6	Comparison of Stripping	88
			Characteristics of TN 2181	
			and Kelex 100	
		5.3.7	Effect of Sn:Rh Molar Ratio	89
		5.3.8	Discussion of Extraction -	92
			Stripping Mechanism	
6.	CONC	LUSIONS	6	97
	6.1	Specia	ition	97
	6.2	Rhodiu	m Extraction Suppression in an	97
		8-Hydr	oxyquinoline Solvent Extraction	
		Circui	t	
	6.3	Extrac	tion of Rh from Rh-Sn-Cl Aqueous	98
		Soluti	ons with 8-Hydroxyquinolines	
API	PENDIC	ES		99
	APPE	NDIX A:	KINETICS	99
	APPE	NDIX B:	CONVERSION OF ACIDITY TO pH - JANSZ	103
	APPE	NDIX C:	Rh EXTRACTION WITH CYANEX 923	106
		C.1	Effect of Acidity and Chloride Addition	106
		C.2	Effect of Acidity with 0.1M SnCl ₂	107
		C.3	Effect of Chloride with 0.1M SnCl ₂	108
		C.4	Effect of SnCl ₂ Concentration on Rh	109
			Extraction	
		C.5	Stripping of Rh-Sn Complex Extracted	110
			by Cyanex 923	
REF	FERENC	ES		112

<u>]e.</u>

LIST OF FIGURES

;

-

2.1:	INCO Precious Metals Refining Flowsheet	4
2.2:	Rhodium Precipitation-Purification Process	6
2.3:	Hexachlororhodate Octahedral Structure	8
2.4:	Reproduction of Moriyama et al's	13
	Distribution Diagram	
3.1:	Reproduction of Cozzi and Pantani's	27
	Rh-Cl Speciation Diagram	
3.2:	Reproduction of Mihailov et al's	28
	Rh-Cl Speciation Diagram	
3.3:	Thermody mamic Speciation Diagram for Rh-Cl	31
	(Based on Cozzi and Pantani's Stability	
	Constants)	
3.4:	Distribution of Rh(III) Chloro-Complexes	33
	at 120°C	
3.5:	Kinetic-Based Rh Chloro-Aquo Complexes	37
	Speciation Diagram	
4.1:	(a)7-Substituted 8 Hydroxyquinoline Derivatives	40
	(b)Tri-Alkyl Phosphine Oxide	
5.1:	Rh Extraction from 0.7 to 8.0M HCl Feeds -	48
	Fresh Solutions	
5.2:	Rh Extraction from 0.7 to 8.0M HCl Feeds -	48
	3 Day Aged Solutions	
5.3:	Ion-Pair Formation Between TN Extractant	50
	and Hexachlororhodate	
5.4:	Reproducibility of Rh Extraction	50
	(Fresh and 3 Day Aged)	
5.5:	Contact Time Effect	51
5.6:	Rh Extraction at $[Cl-] = 4M - Fresh Solution$	53
5.7:	Rh Extraction at $[Cl-] = 4M$	53
	3 Day Aged Solutions	
5.8:	Effect of Total [Cl] on Rh Extraction	55
	(Fresh and 3 Day Aged)	

58 60 61 63 64
60 61 63 64
61 63 64
61 63 64
63 64
63 64
64
64
67
70
75
75
77
80
82
82
84
84
86
88
90
91
ry 96

.

X

- C.1: Schematic of Possible Protonation of TOPO 106
- C.2: Rh Extraction with SnCl₂ and Cyanex 923 108

- C.3: Effect of Cl Concentration in Rh-Sn-Cl/TOPO 109 System
- C.4: Rh Extraction Dependence on the Sn:Rh Molar 110 Ratio in the Feed

LIST OF TABLES

۶ ه

2.1:	Chemical Names and Abbreviations of Some	18
	Common Extractants	
2.2:	Summary of Rh Solvent Extraction Systems	19
2.3:	Summary of Rh Solvent Extraction Systems -	21
	Analytical Determinations	
3.1:	Summary of Stability Constant Data for Rh(III)	30
	Chlorocomplexes	
4.1:	Summary of Extractant Characteristics	40
5.1:	Parameters Investigated with the TN Extractants	46
5.2:	Experimental Results of Reequilbiration Test	72
5.3:	Summary of Exploratory Stripping Tests	79
5.4:	Extraction and Stripping Results for Rh and	87
	Sn Using Recycled 2 Volume% Kelex 100	
A.1:	Calculation of Abundance of Rh Chlorocomplexes	100
	at Various Times in 1M Cl [.] Solutions	
A.2:	Calculation of Abundance of Rh Chlorocomplexes	100
	at Various Times in 4M Cl ⁻ Solutions	
A.3:	Calculation of Abundance of Rh Chlorocomplexes	101
	at Various Times in 6M Cl [.] Solutions	
A.4:	Calculation of Abundance of Rh Chlorocomplexes	102
	at Various Times in 1M Cl ⁻ Solutions	
A.5:	Calculation of Abundance of Rh Chlorocomplexes	102
	at Various Times in 4M Cl ⁻ Solutions	
A.6:	Calculation of Abundance of Rh Chlorocomplexes	102
	at Various Times in 6M Cl ⁻ Solutions	
B.1:	Measured and Calculated Values of HCl, $MgCl_2$	105
	and H^+ to Convert from Concentration to Activity	
C.1:	Summary of TOPO Exploratory Extraction and	111
	Stripping Tests	

<u>CHAPTER 1</u> INTRODUCTION

The separation and purification of rhodium (Rh) from the other precious metals is one of the most difficult and pressing areas in precious metal refining at the present time. This situation arises mainly because of the complex solution chemistry of Rh in chloride-containing aqueous solutions. The complexes, formed by Rh in these types of solutions are such that modern recovery processes such as solvent extraction (SX) which have been implemented for the recovery of the other platinum group metals (PGMs)¹ cannot easily be applied to the recovery of Rh and, to date, no industrially acceptable solvent extraction system has been developed for Rh. The methods which are used for its recovery are therefore very old and inefficient techniques based on a number of precipitation - dissolution stages to slowly and tediously purify Rh.

The main objective of this work was to try to devise and develop a solvent extraction system for Rh which could ultimately be industrially applied. In order to achieve this goal, it was first necessary to acquire an understanding of the behaviour of Rh in chloride-containing solutions.

A secondary objective of this work was to study the behaviour of Rh in a specific solvent extraction system which is to be industrially employed for the recovery of Pt and Pd. In this part of the work, the aim was to develop a technique to inhibit the extraction of Rh in the said system since the coextraction of Rh is undesirable both because it would be an impurity for Pt and Pd and also because the Rh extracted could be lost and never recovered or recovered only at great expense.

Í

¹ The six PGM elements are Pt, Pd, Rh, Ir, Ru and Os.

To present the overall results of this research, this thesis will be divided into three main parts; (i) an overview of the solution chemistry of Rh(III) in chloride solutions as well as an overview of some previous Rh(III) solvent extraction work, thermodynamic and kinetic study of (ii)a Rh(III) chlorocomplexes, and (iii) experimental results and discussion. The results and discussion part will itself be divided in three main categories which include (i) the extraction suppression of Rh(III) in а Pt/Pd 8hydroxyquinoline solvent extraction circuit, (ii) the extraction of Rh(III) using modified 8-hydroxyquinoline systems and (iii) the extraction of Rh from Rh-Sn-Cl aqueous solutions using 8-hydroxyquinoline derivatives. In this last part, a solvent extraction process which offers some promise as a purification/recovery method for Rh from chloride solutions is discussed.

<u>CHAPTER 2</u> <u>LITERATURE REVIEW AND THEORY</u>

2.1. PGM REFINING PRACTICES

Rhodium occurs together in nature with the other PGMs as well as with silver and gold either as native alloys in placer deposits or in lode deposits where they are associated with copper and nickel. It is from the lode deposits that the PGMs are most frequently recovered (1). Because the PGMs occur together, it is important to devise techniques to separate them and to purify and recover each of the metals separately. Originally PGMs were separated after dissolution in oxidizing chloride leach liquors (2, 3, 4) by the application of a precipitation-dissolution steps adopted series of from analytical chemistry methods (5). This was the most common route until about the middle nineteen seventies. Since then, the major refining companies have considerably modernized their processes by implementing the more efficient separation technique of solvent extraction and to a lesser degree, ion Their modernization efforts continue. exchange. Thus, a typical flowsheet incorporating solvent extraction is the one used by INCO Ltd. in Acton, U.K. and it is depicted in Figure 2.1 (3, 4).

2.1.1 Rh Recovery

As depicted in Figure 2.1 and as is the case for virtually all precious metal recovery flowsheets, Rh is the last metal recovered and it is recovered through a complicated precipitation technique rather than through the more modern and efficient technique of solvent extraction. There has, however, been mention of Rh recovery through ion exchange (IX) in one PGM flowsheet (6) but no details have ever been revealed and it is not clear whether or not the ion exchange route is indeed followed.

Figure 2.1: INCO Precious Metals Refining Flowsheet

PGM Concentrate	
Dissolution ————	AgCI
Tetroxide Distillation	Ru/Os
Butex Solvent Extraction	Au
Dioctylsulfide Solvent Extraction	Pd
Reduction of Ir(IV) to Ir(III)	
TBP Solvent Extraction	Pt
Oxidation of Ir(III) to Ir(IV)	
TBP Solvent Extraction	Ir
Rh Purification (Pptn-Dissol'n)	Rh

i.

The precipitation-dissolution scheme for the recovery of Rh is no longer considered satisfactory by most PGM refiners because of its numerous drawbacks. It is a lengthy process, sometimes taking as long as 4 to 6 months for the final recovery of pure Rh metal and therefore, there is a high value of metal which is locked-up in the processing plant. The technique is also quite tedious as the precipitation must be carried out a number of times in order to ensure that the final product is of acceptable purity and this makes the overall process labour intensive and costly. A simplified flowsheet for the Rh precipitation purification scheme is shown in Figure 2.2 (3, 5, 7).

In the precipitation - purification method, the first step involves the formation of the nitrite complex $[Rh(NO_2)_6]^3$ from $RhCl_{4}^{3}$. Because this complex is extremely stable to hydrolysis, the impure Rh-containing solution can be subjected to neutralization with NaOH in order that some of the impurities be precipitated through hydrolysis (3). After a filtration stage, the Rh in solution is precipitated with ammonia and sodium (from the NaOH) as diammonium sodium hexachlororhodate $(Na(NH_4)_{\ell}[Rh(NO_2)_6])$ which is a partially selective precipitation step over the other PGMs which may also be present in the Rh solution. For this precipitation, however, it is important that a high concentration of ammonia be used in order to suppress the solubility of this Rh complex to achieve almost complete Rh precipitation. After another filtration stage, the precipitate is redissolved in HCl and depending on the purity of the solution, the process is started over at the nitriding step.

It is this cycle of precipitation-dissolution stages that renders this process inefficient and tedious. Once the ammonia-nitrite Rh complex is of acceptable purity, the final

dissolution in HCl is followed by the precipitation of Rh with ammonia to give triammonium hexachlororhodate $((NH_4)_3[RhCl_6])$. Here it is not only important that the concentration of ammonia be high to suppress the solubility of the Rh salt but, as well, that the chloride concentration be high since it is the hexachloro-complex which is precipitated and therefore, the hexachloro-complex must be "easily" available in solution. The last step involves the reduction of Rh to the metallic state either directly from this salt with formic acid or with H₂(g) at 1000°C (3,7).

> Figure 2.2: Rhodium Precipitation -Purification Process



Due to Rh's high value (about \$4000 US in mid-1991) and rapidly increasing demand for automobile catalytic converters (8), the need to develop more efficient recovery processes such as solvent extraction for Rh is becoming increasingly urgent. The difficulty in developing such systems, however, lies in the chemical complexity of Rh in chlorid@-containing aqueous solutions. It is part of the subject matter of this thesis to study the intricate solution chemistry of Rh(III).

2.2 THE AQUEOUS CHLORIDE CHEMISTRY OF RHODIUM(III)

It is important prior to reviewing the solvent extraction literature of Rh (Chapter 2.3) to examine the basic characteristics and the behaviour of Rh in chloride solutions because of the peculiar aqueous chemistry of Rh in chloridecontaining solutions.

2.2.1 Basic Inorganic Characteristics

The main oxidation state of Rh is +III although +I and others are known to exist though to a much lesser extent. Also, it has been found that the anionic complexes of rhodium are more labile than those of other PGMs, whereas the cationic and neutral complexes are quite inert.

Rhodium (III) readily forms octahedral complexes, as do most d^6 configurations, with anions, halides, and oxygen-containing ligands. In terms of solvent extraction, it should be remembered that highly charged octahedral complexes such as RhCl₆^{3.} are particularly difficult to extract due to steric effects. It is difficult to pack three organic molecules around a single anion. A schematic diagram of the octahedral structure of RhCl₆^{3.} is shown in Figure 2.3.



Figure 2.3: Hexachlororhodate Octahedral Structure

2.2.2 Rh Species in Chloride Solutions

. . .

A study of the aqueous chemistry of rhodium (III) chloride complexes reveals that a variety of rhodium chloro-aquo complexes exist in solution. Starting with hexachlororhodate ($RhCl_6^{3-}$) substitution reactions of the following kind occur:

$$RhCl_{6}^{3} + H_{2}O \rightarrow RhCl_{5}(H_{2}O)^{2} + Cl^{-}$$
 (2.1)

$$RhCl_{5}(H_{2}O)^{2} + H_{2}O \rightarrow RhCl_{4}(H_{2}O)^{-}_{2} + Cl^{-}$$
 (2.2)

$$RhCl(H_2O)_5^{2+} + H_2O \rightarrow Rh(H_2O)_6^{3+} + Cl^{-}$$
 (2.3)

The species range from the completely aquated hexaaquorhodate, Rh $(H_2O)_6^{3+}$, to hexachlororhodate, Rh Cl_6^{3-} . Mixed aquo-chloro complexes which can be described as $[RhCl_{6-n}(H_2O)_n]^{n-3}$ also exist in equilibrium with each other and with one or both of the above species. The extent to which each complex exists depends primarily on the chloride concentration and also, to some extent, on the temperature, age, and pH of the solution.

It has been found that at pH > 2.9, the chloro-aquo complexes undergo hydrolysis as follows (9):

$$[RhCl_{6-n}(H_{2}O)_{n}]^{n-3} \rightarrow [RhCl_{6-n}(H_{2}O)_{n-1}OH]^{n-1-3}.$$
 (2.4)
where $n \ge 1$

This adds to the number of species which can already be found in a typical Rh chloride aqueous solution.

Also adding to the variety of complexes are chloride- and oxygen-bridged polymeric Rh species thought to be present in aqueous Rh chloride systems (10, 11, 12). Very little is known about these polymeric species and, in the past, they have usually been ignored in both the thermodynamic and kinetic studies performed on aqueous Rh chloride solutions.

2.2.3 Speciation

Because hexachlororhodate is known to be both thermodynamically and kinetically unstable towards aquation, a number of studies have investigated the aquation of rhodium chloride complexes in hydrochloric or chloride-containing solutions. It has been found that at high chloride concentrations, the main rhodium species are $RhCl_6^{3}$ and $RhCl_5(H_2O)^2$ although $RhCl_4(H_2O)_2$ is also known to exist to some lesser extent. As the chloride concentration decreases in an aqueous solution, the aquation reactions occur more easily and extensively. Also, as the temperature of the solution increases, so does the rate of aquation (13). More details on the relative abundance of the various aquochlorocomplexes of Rh(III) (speciation) are presented in Chapter 3. For solvent extraction purposes, it should be remembered that many mixed chloro-aquo complexes exist in solution as a result of aging, total chloride concentration and solution history. Since these various species may undergo ligand substitution at different rates, different complexes exhibiting different extractability may be produced in an aged solution (13). Also, the aquo-containing complexes are particularly troublesome in solvent extraction since not only are they octahedral and therefore quite bulky, but more importantly, these complexes are highly hydrophillic and will not easily be transferred to the organic phase.

2.2.4 Rh in Sulfate Solutions

Because gold is sometimes recovered through the use of SO_2 reduction (14), some PGM refining solutions contain a considerable amount of sulfate. The aqueous chemistry of Rh(III) in sulfate solutions has not been as intensively studied as it has in chloride solutions, however, some Rh-sulfate complexes which have been reported include $Rh_2(SO_4)_3$ and $[Rh(SO_4)_2]^2$ (15).

The studies which have been performed usually start with the dissolution of $Rh(OH)_3$ in H_2SO_4 to obtain, first, $Rh(H_2O)_6^{3+}$ and then, depending on the temperature and sulfate concentration, a number of mixed complexes are formed. These include mixed aquo-hydroxy Rh complexes, mixed aquo-hydroxy-sulfate complexes and oxy-sulfate-bisulfate Rh complexes (9). A whole spectrum of anionic, neutral and cationic complexes may therefore be present in Rh sulfate solutions and more investigations must be performed before a clear determination of the complexes in solution can be presented.

2.2.5 Rh Chloride Complexes and SnCl₂

ł

There has been considerable use made of stannous chloride in the separation and purification of the precious metals using solvent extraction or ion exchange in analytical chemistry (16-23). Because the chloro-complexes of rhodium are relatively inert, and because they often contain aquo ligands, they are not easily extracted. Much more labile and nonaquated complexes of Rh are formed when rhodium chloride complexes are allowed to react with SnCl₂ in acidic solutions.

When SnCl₂ is added in sufficient quantity (greater than a 6:1 molar ratio of Sn:Rh), it reduces Rh(III) to Rh(I) which is more labile than the somewhat kinetically inert chloride complexes of Rh due to the strong π -acid nature of the SnCl₁. ligand (16). The replacement of $SnCl_3$ by another ligand is not subject to such kinetic difficulties as is the replacement of chloride as a ligand (17). The structure of the Rh(I)-SnCl₁ complex has been investigated by а number of researchers. One structure which had originally been proposed is a bridged Rh(I) dimer such as $[Rh_2Cl_2(SnCl_3)_4]^{4}$ (9, 24). More recently, however, this species was rejected and the simple anion $[Rh(SnCl_3)_s]^4$ was adopted (12). Nevertheless, one or both structures are still reported in many articles and the exact structure has still not been clearly determined or unanimously adopted.

When $SnCl_2$ is **not** added in significant excess of Rh, then the complexes formed are quite different. An extensive study of the complexes formed by allowing RhCl₃·3H₂O to react with SnCl₂ (Sn:Rh molar ratio 6:1 or less) in 3M HCl was performed through ¹¹⁹Sn NMR spectroscopy (12). Complexes of the type $[Rh(SnCl_3)_nCl_{6:n}]^{3\cdot}$ (n = 1-5) have been identified as well as the Rh(I) complex which was described as $[Rh(SnCl_3)_5]^4$. A possible formation reaction for the Rh(III)-Sn complexes is given below.

$$[RhCl_{6-m}(H_2O)_m]^{n\cdot3} + mSnCl_3^- \rightarrow [RhCl_{6-m}(SnCl_3)_m]^{3\cdot} + m-nCl^- + nH_2O$$
(2.5)

For the Rh(I) complex, a possible formation reaction may be:

$$\operatorname{RhCl}_{6}^{3} + 6\operatorname{SnCl}_{3}^{-} \rightarrow [\operatorname{Rh}(\operatorname{SnCl}_{3})_{5}]^{4} + 3\operatorname{Cl}^{-} + \operatorname{SnCl}_{6}^{2} - (2.6)$$

The Rh(I) complex is known to be relatively unstable in solution and it may convert back to one of the Rh(III)-Sn-Cl complexes on standing if Sn(II) is not in sufficient excess (12). However, if excess SnCl₂ is present, then the Rh(III)-Cl-Sn complexes will slowly be converted to the Rh(I) species $[Rh(SnCl_3)_5]^4$ (25). It has been found that this Rh(I) species is the most abundant when the Sn:Rh ratio is greater than 4:1. The existence of various complexes helps to explain the change in colour of the aqueous solution from orange to dark purplered as the Sn:Rh ratio increases.

The exact solution composition for a Rh-Sn-Cl system is obviously quite complex and it depends on a number of factors such as the Rh:Sn solution ratio, temperature, age of solution, and possibly HCl or chloride concentrations since the chloride ion concentration will affect the speciation of the Sn(II) chloride complexes from Sn^{2+} to SnCl_4^{2-} . A speciation diagram for the various Rh-Sn complexes present in solution at 25°C and in a 3M HCl solution as a function of the Sn:Rh complex ratio is given in reference 12 and is reproduced in Figure 2.4.

It is interesting to note that when the Sn:Rh solution molar ratio is 6 or less, it has been found that there is no free Sn(II) in solution. In 3M HCl, the reaction between the Rh complexes and SnCl₃⁻ is complete since no free Sn(II) can be detected in solution until more than the stoichiometric amount



1

ł

1. RhCl³⁻ 5. Unassigned

- 2. Rh(SnCl_3)Cl_ $^{3-}$ 6. Rh(SnCl_3)₄Cl_2^{3-}
- 3. Rh(SnCl₃)₂Cl³⁻ 7. Rh(SnCl₃)₆Cl³⁻
- 4. Rh(SnCl₃)₃Cl₃³⁻ 8. Rh(SnCl₃)₄⁴⁻

Figure 2.4: Reproduction of Moriyama et al's Distribution Diagram (ref. 12)

of Sn:Rh (6:1 for complete reduction and ligand substitution) has been added. This means that all of the Sn(II) which is added to the Rh solution is immediately used to become either part of the Rh complex or, to reduce Rh(III) to Rh(I).

Having stated that highly charged octahedral complexes are difficult to extract, it might seem that the formation of a 4. complex would cause more problems than it would solve. It seems, however, that this complex is much more labile than the Rh(III) chloride complexes and therefore it may react much more readily with various organic extractants. Also, the Rh-Sn-Cl complexes are not aquated so they are not nearly as hydrophillic as the mixed aquo-chloro complexes of Rh(III). The fact that there are only 5 ligands coordinated to the Rh(I) might also explain the apparent high reactivity of this complex since it is possible that Rh wants to complete either it's Rh(III) usual octahedral symmetry or the Rh(I) d⁸ squareplanar symmetry and so it reacts quickly with the extractant. Finally, it is also apparent that [Rh(SnCl₃)₅]⁴ is larger than the Rh(III) aquo-chloro complexes and therefore it might be easier to surround this species with the organic molecules than it is the smaller Rh(III)-Cl-H₂O complexes.

2.3 SOLVENT EXTRACTION

2.3.1 Solvent Extraction

Successful development of a solvent extraction process for Rh refining is expected to bring a number of advantages over the conventional refining practice. For example, the capital and operating costs are expected to be lower, the overall processing time to be much lower and therefore there is not such a large amount of metal and capital investment which is locked in process in the plant. As well, it does not require as much

physical manipulations and personnel. The use of an effective solvent extraction process should also allow for greater flexibility in the overall process flowsheet. Finally, the effluents may be less problematic than those obtained from the more cumbersome precipitation - dissolution technique.

For a solvent extraction process to be considered as industrially acceptable, some criteria governing solvent extraction processes must be met (11). For example, the extractant must be stable and the metal extracted must not cause excessive reagent degradation. The extraction stage must be quite selective and have a high distribution coefficient $(D_x>10^2)$ and essentially complete stripping must be achieved $(D_u>10^2)$. The stripping reagents should be as simple as possible and the media should be such that the purified metal can be easily and directly recovered. To date, no such system has been developed for Rh.

2.3.2 Solvent Extraction with Amines

Í

There have been a number of studies on the extraction of Rh and the other PGM with various organic amine extractants and an overview can be found in reference 26. It has been found that although Rh can be extracted under certain conditions, the other PGM are usually more readily extracted than Rh and therefore, amines are useful to extract Rh only if it is the only precious metal in solution. All amines are capable of extracting a number of base metals and therefore, selectivity can be a problem.

In general, the extraction of Rh is favoured at low acidity and low chloride concentrations. In the precious metal refining industry, the total chloride concentration is usually quite high (4M) as is the acidity although it can $b \ge easily$ adjusted. Studies performed with tri-n-octlyamine (22, 27) have shown that Rh is only significantly extracted at 0.1M HCl. At HCl concentrations of 1 to 12 M, the extraction drops to zero. Another study on tri-isobutylamine (26) has shown that Rh is not significantly extracted from solutions up to 5M in HCl concentration.

There have also been some studies performed on the extraction of precious metals with primary amines (23). Rh(III) can in fact be extracted by primary amines from aqueous solutions when the acid concentration is quite low (<0.5M HCl) but other PGMs are also extracted. The extraction of precious metals with amines is believed to be generally represented by the following reactions:

$$R_3N + HC1 \rightarrow R_3NH^+C1^-$$
 (2.7)
 $3R_3NH^+C1^- + MC1_6^{3-} \rightarrow (R_3NH)_3MC1_6 + 3C1^-$ (2.8)

For Rh, however, the extraction reaction is believed to be more complex. It has been speculated that the Rh complex which is extracted with amines is $RhCl_5(H_2O)^2$. Because of the hydrophilicity of this species, it does not remain in the organic phase as this species but rather, it is believed to undergo rapid dimerization or possibly polymerization (3) as, for example, in the following reaction:

$$2(R_4N)_2[RhCl_5(H_2O)] \rightarrow (R_4N)_3[Rh_2Cl_9] + R_4N^+Cl^+ + 2H_2O$$

(2.9)

The $Rh_2Cl_9^{3-}$ anion is so strongly extracted that it is then "locked-up" in the organic phase and stripping is impossible.

An investigation of the kinetics of extraction of Rh from chloride solutions with a quartenary ammonium chloride extractant was recently performed (29). An extraction degree of about 80% was obtained under the best conditions tested (25°C, $[H^+]=1M$, $[Cl^-]=1M$). Stripping and selectivity were not studied, however, and as explained above, these can be expected to cause problems. As with the other amine extractants, the extraction degree increased with decreasing acidity and chloride concentration.

ŝ.

ŕ

The drop in extraction degree with increasing chloride ion concentration can be explained by considering reactions 2.7 and 2.8. It is clear that the extraction of the precious metal species is based on an anion exchange reaction between the chloride ion and the negative metallic complex. If the concentration of chloride ion is too high, then its replacement by the metal anion will become more and more difficult and the extraction degree will drop. In fact, one of the stripping reagents which can be used to strip the precious metals from loaded amines is a concentrated chloride ion solution (3).

2.3.3 Summary of Other Solvent Extraction Studies

A number of studies examining different extractants have previously been published (17-42). Although there exist a number of solvent extraction systems for the extraction of Rh from mixed PGM solutions in neutral or acidic aqueous solutions, these systems cannot be used as designed for the industrial extraction of Rh. Many of the known solvent extraction systems were developed as analytical tools for the determination of Rh concentration by spectrophotometric methods, and the experimental procedures performed on the solutions to achieve extraction are not feasible from an industrial point of view. For example, the solutions must often be heated to boiling and evaporated to dryness. The time and energy requirements for this process are not practical in industry.

Γ

Other 'olvent extraction systems are designed to extract the cationic complexes of Rh(III). Again, from the refining point of view, this is not practical since the industrial Rh aqueous solutions usually contain high levels of chloride and therefore, the predominant species can be expected to be the anionic chloro-aquo complexes of Rh. Diluting the solutions down to such a point that the cationic complexes dominate is not a realistic option for a number of reasons.

Nonetheless, it is useful to be aware of the solvent extraction systems studied by other researchers. Tables 2.1 to 2.3 briefly summarize the main results obtained in these previous studies.

Table 2.1: Chemical Names and Abbreviations of Some Common Extractants

<u>Abbreviation of</u> Extractant	Full Chemical Name
N ₂₃₆	trialkyl methyl ammonium chloride
TOA	tri-n-octyl amine
TBP	tributylphosphate
TOPO	trioctyl phosphine oxide
TPPS	triphenyl phosphine sulphide
TBPS	tri-n-butyl phosphine sulfide
THPS	tri-n-hexyl phosphorothioic-triamide

Table 2.2: Summary of Rh Solvant Extraction Systems (X = extraction)

Ĺ

<u>Extractant</u> (Aqueous Medium)	Complex Extracted	General Comments	<u>Ref.</u>
N _m , (2M HCl) (Trialkyl methylammon- ium chloride) Alkyl is 8-10 C-chain	3N ₂₀ +2RhCl ₆ = (R ₃ CH ₃ N) ₃ Rh ₂ Cl ₉ + 6Cl ⁻	Direct X without pretreatment. X=f([N _{xs}],[H ⁺] ⁻¹ , [C1 ⁻] ⁻¹ , T, age ⁻¹). Max of 80% X at [H ⁺] and [C1 ⁻] = 1. No mention of selectivity or stripping.	29
Tri-n-octyl- amine (TOA) in benzene	Rh-Sn-Cl	Solution heated for 1 hr prior to X. No mention of stripping.	22
(TOA) (0.1-10M HCl)	Rh-Cl	Without SnCl ₂ , max X of 85% and only in (0,1M) HCl. (at >4M HCl,no X)	22
Tri-n-octyl- amine in benzene (0.1 -12M HCl)	Rh-Cl	Not significantly Xed at > 0.1M HCl. X decreases with increasing (HCl). About 75% X at 0.1M HCl.	27
Primary amine in kerosene (0.3-2.5M HCl)	Rh-Cl	X deceases with increasing [HC1]. Not selective w.r.t. PGMs and Cu, Fe and Ni. Good stripping and X under favorable conditions. Presence of $SO_4^{2^\circ}$ is detrimentation X degree.	28 1
Mono-N-amide (RHNCOR') Strong HCl		For Ir X over Rh(III). Rh not Xed.	30
Benzoylphenyl- hydroxylamine (1-9M HCl)	Rh-Sn	Not selective. 100% X from 1-3M HCl	18
Dinonylnaph- thalene sul- fonic acid in n-heptane (Weak HCl)	Rh(H ₂ O) ₆ ³⁺	Liquid cation exchanger. 90-95% recovery. Relatively good selectivity except for Ru. Probably X only aquated Rh. Strip with 6M HCl.	31
Di-n-heptyl sulfoxide (DHSO; in 1,1,2 trichloroethane	Not stated	Max 60% X at 30 min CT. Not selective. To strip, need NaNO ₂ at 70°C and at $pH=7$. Other sulphoxides and sulphides also tested but no greater X.	32

<u>Extractant</u> (Aqueous Medium)	Complex Extracted	General Comments	<u>Ref.</u>
Tributyl phosphate (TBP) (1-9M HCl)	Rh-Cl	Max of 16% X only.	33
TBP (pH 1-4)	Rh(SCN) ₆ ³	Not selective and even better for Pt, Pd and Ir. TBP degrades to DBP after some time. Need KSCN:Rh ratio of 200:1 to get significant X.	34
TOPO in toluene (HCl:.01-10M)	Rh	Not Xed to any sig. degree. Not selective.	35
Dichloro- ethane and diantipyryl- propylmethane (1M HCl)	Rh chloride complexes	Not selective for Rh. Tested for small quantities. To strip, need 25% HNO3	36
TPPS, TBPS, THPS in HNO ₃	Rh (NO ₃) 6 ¹⁻	CT from 3-6 hrs. Solvating mechanism proposed for THPS. HNO, also Xed so may get acid build-up in extractint. No X in HCl media. No X with TPPS.	37
Triphenyl- phosphine in dichloroethane (1-5 M HCl)	Rh-SnCl,	No X without $SnCl_2$. With $SnCl_2 - 100$ % X. Need to heat aqueous phase on H ₂ O bath for 30 min. Not selective. No stripping performed. Solvation mechanism proposed.	17
Dinonlynaph- thalene (0,1 to 1M HNO ₃)	Rh(H ₂ O) ₆ ³⁺ Cr Rh(H ₂ O) ₅ NO 2 ²⁺	CT about 5 min. No X in HCl. Good X in HNO ₃ . Selectivity not studied. Strip with 2-3 M HNO ₃ .	38
Diphenyl- thiourea 6M HCl	Rh-Cl ₂ (DPTU)	No X without $SnCl_2$. Extracts other PGMs also. Stripping not studied.	39
Salicyl- hydroxamic acid (pH 5-6.5)	Rh	Selectivity and stripping not tested. X high (>50%) only above pH 5.5 so not good in acid.	40

J

4

- ر

Table 2.3: Summary of Rh Solvent Extraction Systems - Analytical Determination (X = extraction)

<u>Extractant</u> (Aqueous Medium)	Complex Extracted	<u>General Comments</u>	<u>Ref.</u>
Chloroform/ acetone (3:2) (1-2M HCl)	Diphenylthio- urea Sn-Rh-Cl complex.	Use of CHCl ₃ without acetone gives a skin at A/O interface. Long procedure.	19
Ethylacetate (2-4M HCl)	l-phenyl 3- thiobenzyl- thiocarbamide Sn-Rh-Cl	No X without SnCl ₂ . 63% X in H ₂ SO ₄ . Other organics produced a third phase.	20
MIBK (3-6M HCl)	2-mercapto- benzothiazole Rh complex.	Used for UV analysis. Complete X in 3-6 M HCl. Rh and Ir Xed together.	41
Chloroform (0.2-2M HCl)	2-mercaptoben- zothiazole-Sn- Rh complex	Method to X Pt, Pd and Au at same time as Rh.	21
Chloroform (4-6M HCl)	same as above	Used for AA analysis.	42

2.3.4 Ion Exchange

ł

Ion exchange (IX) technology will not be reviewed extensively as it is beyond the scope of this work, however some general points are discussed below. Two review articles intended specifically for analytical chemists describe the separation of Rh from the other PGMs using IX techniques (13, 43). There has been some work done on IX in the hope of developing a system for industrial Rh recovery applications. In fact, it was reported that Matthey Rustenburg may be using an IX process in their Rh recovery operations (6) but details have never been published and it is not known whether or not an IX process is indeed being used.

As with SX, most IX systems which can extract Rh also extract other PGMs and therefore, they can only be used if no other PGMs are present in solution. Some of the resin types which have been investigated include strong base anion exchange

resins (6, 40) and thiourea based resins (43) neither of which are selective for Rh. Other less common types of resins such as polyurethane foams (16, 23) and some cation exchange resins (44) have also been studied. Indeed, there seem to exist quite suitable systems for the recovery of Rh in it's cationic form in the presence of other precious metals and base metals but these apply only to non-chloride solutions. In refining, strong chloride solutions are usually used and in these solutions, as has already been discussed, Rh exists as anionic chloro complexes.

Recently a newer class of separation molecules which resemble IX resins have been developed for Rh recovery. These are based on crown ethers and are described as molecular recognition ligands (45, 46). The functional molecule which bound to a solid silica support, is designed and is synthesized in order to selectively bind a specific metal species by carefully considering its geometry, size, charge and coordination affinity. A resin-like material called Superlig[™] 1, able to separate Rh(III) and Ir(III) from the other PGMs and some of the base metals in chloride solutions, was recently described (46). The complexes which are extracted are the hexachloro-Ir and Rh complexes. This material is therefore believed to be more useful when separating Rh and Ir from highly concentrated chloride solutions since it is only in these solutions that the hexachloro-complexes are predominant as explained later and as depicted in Figure 9.

SuperLigTM 1 offers a significant amount of selectivity and rapidity which makes possible its application at the head of the PGM flowsheet rather than at the end. Its drawbacks are that some Pt and Pd will be coextracted along with Rh and Ir and also, the Rh and Ir are extracted and eluted together. The Rh and Ir must then be separated by some other method.

Its main drawback, however, lies in the complex elution scheme which is required to completely strip the Rh and Ir from the co-extracted Pt and Pd. Depending on whether the Rh and Ir are eluted separately or concurrently, the main elution solutions are ethylenediamine at pH 1 and ethylenediamine at pH 10 with the simultaneous application of heat at a highly controlled temperature profile. Also, as the material is not resistant to strong bases (pH>11) , the pH 10 elution stage must be well monitored to make sure that the alkalinity never rises to pH 11.

'n

í
CHAPTER 3 SPECIATION ANALYSIS AND DETERMINATION

In terms of developing a solvent extraction process for Rh(III), it is very important to know both the specific Rh complexes present in solution and their relative abundance since cationic, anionic and neutral species are not extracted via the same mechanism or with the same type of extractant. Only by knowing this information will it then be possible to choose the best type of extractant. A speciation diagram for Rh with chloride ion as the complexing ligand is most useful for obtaining this type of information.

Although speciation diagrams are relatively common for many elements, for Rh in chloride solutions, the lack of reliable and reproducible thermodynamic stability data results in few diagrams being available. It was therefore considered important to critically evaluate those which are, and to try to determine if any previously published data could be used to construct a new, more reliable speciation diagram.

3.1 Speciation Diagrams

For the speciation diagrams for Rh in chloride aqueous solutions, seven complexes are considered and these are $Rh(H_2O)_6^{3+}$, $RhCl(H_2O)_5^{2+}$, $RhCl_2(H_2O)_4^+$, $RhCl_3(H_2O)_3$, $RhCl_4(H_2O)_2^-$, $RhCl_5(H_2O)^{2-}$, and $RhCl_6^{3-}$. The hydrolysed species mentioned previously which are believed to be present at pH > 3 will not be considered here since it can be assumed that industrial feeds generally have acidities where pH < 3. The chloride and oxygen bridged polymeric Rh species thought to exist in Rh chloride systems will also be ignored since no kinetic or thermodynamic data of any kind are available in the literature and therefore it is impossible to treat and include these species in a speciation diagram.

It would be useful at this point to briefly describe how a speciation diagram is constructed. Speciation diagrams are based on the stability constants for all the species present in solution. For example, for the Rh species, the stability constants are:

$$K_{1} = \underbrace{[RhC1^{2+}]}_{[Rh^{3+}][C1^{-}]} K_{2} = \underbrace{[RhC1_{2}^{+}]}_{[RhC1^{2+}][C1^{-}]} \dots K_{6} = \underbrace{[RhC1_{6}^{3-}]}_{[RhC1_{5}^{2-}][C1^{-}]} 3.1$$

or alternatively,

$$K_{1} = \underbrace{[RhC1^{2+}]}_{[Rh^{3+}][C1^{-}]} \quad \beta_{2} = \underbrace{[RhC1_{2}^{+}]}_{[Rh^{3+}][C1^{-}]^{2}} \quad \cdots \quad \beta_{6} = \underbrace{[RhC1_{6}^{3-}]}_{[Rh^{3+}][C1^{-}]^{6}} \quad 3.2$$

where K's are referred to as stepwise stability constants and β 's are overall stability constants. Please note that the H₂O ligands are not written but are, of course, present.

The total Rh concentration for any solution can easily be determined and it is defined as:

$$[Rh]_{tot} = [Rh^{3+}] + [RhCl^{2+}] + [RhCl_{2}^{+}] + \dots + [RhCl_{6}^{3-}] 3.3$$

and therefore,
$$[Rh]_{tot} = [Rh^{3+}] + K_{1}[Rh^{3+}][Cl^{-}] + \beta_{2}[Rh^{3+}][Cl^{-}]^{2} + \dots + 3.4$$
$$\beta_{6}[Rh^{3+}][Cl^{-}]^{6}.$$

Clearly if all of the stability constants and the total Rh concentration are known, it would be possible to solve the above equations at any given chloride ion concentration to determine the amount of each species present in solution.

It is important here to recall that the thermodynamic stability constants are expressed in terms of activities while the mass or concentration stability constants in terms of concentrations (47). Therefore, the relevance of the speciation diagrams to real industrial solutions greatly

depends on the source and type of stability constant data.

A speciation diagram for the seven complexes of Rh mentioned above has been constructed by Cozzi and Pantani (48), who based their diagram on six stability constants calculated from polarographic data they obtained. A reproduction of their speciation diagram can be found in Figure 3.1. (Please note that $[H^+] = 1M$).

The polarographic data published by Cozzi and Pantani was reanalysed by Mihailov and coworkers (49) using a mathematical model developed by Mihailov (50) to treat polarographic data. Even though the same experimental results were used, their method gave rise to significantly different stability constants from those calculated by Cozzi and Pantani and therefore to a different speciation diagram. A reproduction their speciation diagram is shown in Figure 3.2.

Obviously, there is a significant difference between the two sets of stability constants calculated and therefore the speciation diagrams obtained are also very different even though all of the results are based on the same polarographic data.

The differing methods used to calculate the constants explains the variations obtained. Cozzi and Pantani used Ford and de Hume's method (51) to calculate stability constants for $Rh(H_2O)_6^{3+}$, $RhCl(H_2O)_5^{2+}$ and $RhCl_2(H_2O)_4^+$ because this method is especially suited for those complexes that are significantly present at very low ligand concentration. However, because the stability constants are not calculated simultaneously with this method, the error incurred in calculating the previous stability constant is carried over to all of the following constants. Cozzi and Pantani then used Riccoboni's method





C.

a de la composición de la comp

Figure 3.2: Reproduction of Mihailov et al's Rh-Cl Speciation Diagram



log [Cl]

(52) which allows for the simultaneous calculation of the constants to calculate the last three constants. The six stability constants obtained by Cozzi and Pantani are given in Table 3.1 found below.

Mihailov et al (49), on the other hand, have calculated only five stability constants (β_1 to β_5) since for their model to "fit" the data only five constant: could be obtained. Of course, the problem with this is that six stability constants are required if all species are to be taken into account. To overcome this problem Mihailov et al chose to consider the tetrachloro and pentachloro species as being one (β_4 for the speciation diagram) and they consider hexachlororhodate to have the stability constant referred to as β_5 .

The first effect of this is to greatly increase the predominance of $RhCl_6^{3-}$ by making it the dominant species at chloride ion concentrations as low as $\approx 0.08M$. Another obvious effect is that the amount of $RhCl_5(H_2O)^{2-}$ or $RhCl_4(H_2O)_2^{-}$ is not determined alone but rather as the sum of the two so that, in fact, this cannot be considered to be a true speciation diagram. Finally, one of the most important points is that in all of the other (see Table 3.1) complex stability studies which have been performed, the stepwise stability constant for $RhCl_6^{3-}$ (K₆) is always less than 1. This implies that below a chloride concentration of 1M, $RhCl_6^{3-}$ cannot be more prominent than $RhCl_5(H_2O)^{2}$ whose stability constant is greater than 1. In this diagram, however, $RhCl_6^{3-}$ is clearly the most dominant species at chloride ion concentrations much less than 1M and this casts a shadow of doubt on the overall diagram. For these reasons, it would be wise to keep a critical perspective and avoid the use of Mihailov's speciation diagram.

Although these two studies are the only ones that give stability constants for all the complexes, there have been other studies that calculate stability constants for just one or two species. The following table lists all of the constants determined for various ionic strengths and temperatures and which are referred to in some of the main stability constant reference books.

Table	3.1:	Summary	of complexes	stabili	ty co	nstant	data	for	Rh(III)-
T K	I (M or	m)		<u>log</u> !	K				<u>Ref.</u>	
298	1.0	K ₁ =2.45	K ₂ =2.09	K ₃ =1.38	K ₄ =1.16	K ₅ =1.67	K ₆ ≖-0.3	2	48	
308	4.0						$K_6 = -1.1$		53	
298	1.0	K ₁ =2.62	$\beta_2 = 4.38$	$\beta_3 = 5.94$	$\beta_4 = 7.42$	β ₅ =8.79			49	
298	0.1				K ₄ =1.39	K ₅ =0.55	K ₆ ≕-0.2	23	54	
288 293 298 308 303 308 313	4 4 4 4 4						$K_6 = -0.7$ $K_6 = -0.8$ $K_6 = -0.9$ $K_6 = -1.1$ $K_5 = 0.90$ $K_5 = 0.83$ $K_5 = 0.80$	2 2 3 4	55 55 55 56 56 56	
318	4						$K_5 = 0.77$		56	
348 353 358 291	2.5 2.5 2.5 var	$K_1 = -0.0$ $K_1 = -0.1$ $K_1 = -0.1$	5 0 5				K ₆ <−0.3		57 57 57 57	
393	6.0	к ₁ >3.0	K ₂ >3.0	K ₃ ≈3.0	K ₄ =2.4	K5=1.4	$K_6 = -0.2$	5	57	

It is quite apparent that there is limited data available from the literature for stability constants for Rh chloride complexes and that which is available is often inconsistent. Despite these limitations, the data can be used as a guide but with caution. For example, all of the data for K_6 indicate that the stability constant is less than one and therefore it is reasonable to expect that at one molar total chloride

Figure 3.3: Thermodynamic Speciation Diagram for Rh-Cl Based on Cozzi and Pantani's Stability Constants



Ĺ

ý

concentration, $RhCl_5(H_2O)^{2-}$ is more dominant than $RhCl_6^{3-}$. Finally, for the reasons mentioned previously and because of their completeness, Cozzi and Pantani's data was chosen to regenerate the diagram of Figure 3.3 in the region of chloride ion concentration of interest to PGM refining scientists. The effect of temperature on the Rh(III) speciation can be calculated with the data reported for $120^{\circ}C$ and i=6 (57). With the use of the data, the diagram in Figure 3.4 was constructed. Despice the previously mentioned trend (13) of enhanced aquation at elevated temperatures, the results of Figure 3.4 do not seem to confirm this to any great extent with the minor exception of $RhCl_4(H_2O)_2$ whose presence seems Of course, it should be remembered that the to increase. diagram of Figure 3.4 does not consider how the kinetics are affected by temperature.

3.2 Kinetics of Aquation/Anation

Although equilibrium speciation diagrams are important and useful, it is also important to remember that the kinetics of ligand exchange between chloride and aquo ligands is just as important. How quickly a solution reaches the equilibrium conditions which can be described in speciation diagrams determines whether or not the diagram will be useful to evaluate a given Rh solution's composition.

Because the industrial solutions from which Rh is to be recovered are relatively concentrated in terms of chloride ions, it is obvious that the species most abundant in solution are $RhCl_4(H_2O)_2$, $RhCl_5(H_2O)^{2-}$ and $RhCl_6^{3-}$ (see Figure 3.3). It therefore follows that the rates of aquation (the exchange of a chloride ligand for an aquo ligand) and the rates of anation (the exchange of an aquo ligand for a chloride ligand) for these three complexes are quite important.

Figure 3.4: Distribution of Rh(III) Chloro Complexes at 120°C



(

There has in fact been a kinetic study performed on the following reaction (in 4M HCl) (55):

$$RhCl_6^{3-} + H_2O = \frac{k_1}{k_2}$$
 $RhCl_5(H_2O)^{2-} + Cl^{-}$ 3.5

and the following kinetic equation was determined

$$-\underline{d[RhCl_6^{3-}]} = k_1[RhCl_6^{3-}] - k_2[RhCl_5(H_2O)^{2-}][Cl^-]$$
 3.6
dt

where
$$k_1 = 0.11 \text{ min}^{-1}$$

 $k_2 = 0.013 \text{ min}^{-1} \text{ M}^{-1}$
at T = 298 K
and t = time in minutes

Similarly, the kinetics of the second aquation reaction have been studied (in solutions of up to 0.4M HCl) (56).

RhCl₅ (H₂O)²⁻ + H₂O
$$\frac{k_3}{k_4}$$
 RhCl₄ (H₂O)₂⁻ + Cl⁻ 3.7

The following rate equation was determined:

$$-\underline{d[RhCl_{5}(H_{2}O)^{2^{-}}]} = k_{3}[RhCl_{5}(H_{2}O)^{2^{-}}] - k_{4}[RhCl_{4}(H_{2}O)_{2^{-}}][C1^{-}]$$
 3.8
dt

where $k_3 = 4.8 \times 10^{-3} \text{ min}^{-1}$ $k_4 = 3.84 \times 10^{-2} \text{ min}^{-1} \text{ M}^{-1}$ T = 298 Kand t = time in minutes

Please note that the k_3 and k_4 values given here were calculated using the Arrhenius equation from rate constants reported (56) from 30°C to 45°C.

It is useful to notice that the aquation of $RhCl_6^{3}$ occurs more rapidly than that of $RhCl_5(H_2O)^{2}$ and this trend continues as the number of chloride ligands decreases. Conversely, the anation of chloride ligands occurs more rapidly in the $RhCl_4(H_2O)_2^{-1}$ complex than in the $RhCl_5(H_2O)^{2-1}$ complex.

At this point, it becomes important to compare the thermodynamic predictions to the kinetic predictions. First, should be equivalent to the kinetic equations the thermodynamic predictions after a suitably long period of time $(at -d[RhCl_n]/dt = 0)$. For the first ligand exchange reaction (3.5), this is obviously not the case since kinetics show that at, for example, chloride ion concentrations of 4M, the amount of $RhCl_{6}^{3}$ in solution at equilibrium is 32% while the thermodynamic speciation diagram (Figure 3.3) shows 70% (Mihailov's diagram predicts 100%). Obviously then, the kinetic data contradict the corresponding equilibrium speciation data.

Since the kinetic and thermodynamic predictions are so different, it would be interesting to see what a modified speciation diagram for Rh would look like using, this time, the kinetic values. In other words, the equilibrium state is defined on the basis of the rates of the ligand exchange reactions rather than on the basis of the stability constants of the complexes. For this only the three anionic species will be considered since in solutions with more than 0.5M chloride ion only these three species are believed to dominate (see Figures 3.1 and 3.2). The calculation is done at 25°C.

It is possible to calculate the stability constants from the kinetic rates in the following manner:

$$\frac{-d[RhCl_{6}^{3}]}{dt} = 0 \text{ and therefore,} 3.9$$

$$0 = k_1[RhCl_6^{3^-}] - k_2[RhCl_5(H_2O)^{2^-}][Cl^-]$$
 3.10

so,
$$K_6 = \frac{[RhCl_6^{3-}]}{[RhCl_5(H_2O)^{2-}][Cl^-]} = \frac{k_2}{k_1} = \frac{0.013}{0.11} = 0.12$$
 3.11

Similarly,

$$K_{5} = \frac{RhCl_{5}(H_{2}O)^{2}}{[RhCl_{4}(H_{2}O)_{2}][Cl^{-}]} = \frac{k_{4}}{k_{3}} = \frac{3.84 \times 10^{-2}}{4.80 \times 10_{-3}} = 8$$
 3.12

Also we know for this case that the total Rh can be expressed as follows:

$$[Rh]_{tot} = [RhCl_4] + [RhCl_5^2] + [RhCl_6^3]$$
 3.13

$$= [RhCl_{4}] + K_{5}[Cl][RhCl_{4}] + K_{5}K_{6}[Cl]^{2}[RhCl_{4}] \qquad 3.14$$

Using the kinetic-based stability constants the speciation diagram of Figure 3.5 was prepared. In the computation of the kinetic speciation diagram, the simultaneous rate equation for

$$RhCl_{6}^{3-} \xrightarrow{4} RhCl_{5}(H_{2}O)^{2-} \xrightarrow{4} RhCl_{4}(H_{2}O)_{2}^{-}$$
 3.15

was not taken into account because the formation of $RhCl_4(H_2O)_2^-$ does not occur to such an extent, in the chloride ion concentration region of interest (>0.5M), such as to have an appreciable effect on the overall distribution of $RhCl_5(H_2O)^{2-}$ and $RhCl_6^{3-}$.

This "kinetic" speciation diagram (Figure 3.5) is obviously quite different from those obtained in the literature and which were shown previously, however, it is in close agreement with that reported by Grant (3). The crossover point for $RhCl_6^{3}$ and $RhCl_5(H_2O)^{2}$ for this "kinetic" diagram occurs at about 8.7M chloride ion, for the diagram of Cozzi and Pantani at about 2.2M and for the diagram of Mihailov et al at about 0.04M.

The kinetic-based speciation diagram is in fact a pseudoequilibrium diagram where the experimentally determined kinetic ligand exchange rates have been converted to stability constants and to a distribution diagram. It is believed that



Ĺ

this diagram is the most industrially useful diagram since in refining, true equilibrium is not as important as practical equilibrium (for example, one week old solutions) and solution composition.

Cozzi and Pantani's thermodynamic distribution diagram (Figures 3.1 and 3.3) may in fact represent more closely what exists at the true equilibrium, however, error in this diagram, which is based on polarographic data obtained in the 1950's, may also be present.

It seems unlikely, however, that the diagram proposed by Mihailov et al is correct since it has been experimentally observed in the laboratory that $RhCl_6^{3}$ solutions of 0.7M chloride ion quickly undergo a colour change from dark red to orange-red to light orange. This is highly indicative of the aquation reactions which according to Mihailov's diagram should hardly be present at such chloride concentrations.

Until more reliable experimental results are obtained for the thermodynamic stability constants for all of the Rh chloroaquocomplexes, it is believed that the kinetic-based distribution diagram is useful in evaluating a given solutions composition after a suitable period of aging and in relatively strong chloride solutions. Finally, it should be noted that according to the rate constants of the aquation/anation reactions, virtual equilibrium is reached rather quickly. This is demonstrated in Appendix A where some key calculations are performed.

<u>CHAPTER 4</u> EXPERIMENTAL PROCEDURE

4.1 Reagents

, in the second s

ſ

Various organic extractants were used in the course of this investigation and these can be divided into two main groups, either 8-hydroxyquinoline derivatives (TN 1911, TN 2181 and Kelex 100)² or a tri-alkyl phosphine oxide reagent (Cyanex 923)³. TN 1911 (lot 05/04/1078) and TN 2181 (lot number not provided) are research products and were provided by Schering Berlin A.G. (Germany). Kelex 100 (lots 3349-72 and 3349-142) was supplied by Sherex Chemical Co. (Ohio, USA), a subsidiary of Schering Berlin. Cyanex 923 is a product of Cyanamid Co (Niagara Falls, Ontario). Another extractant, Versatic Acid 10 (a Shell Chemical UK Ltd product) was used for one set of experiments during the course of this work. Versatic Acid 10 is a carboxylic acid based extractant whose chemical structure can be described as $(CH_3)(C_2H_5)(C_5H_{11})CCOOH$. More data on the reagents are presented in Table 4.1. The chemical structure of the two main classes of extractants used can be found in Figure 4.1.

³ Proprietary product of Cyanamid Co.

² Proprietary products of Schering Berlin A.G. and Sherex Co.

Type of Extractant	Trade Name	R group	Average mol.Wt.	Purity
	Kelex 100 (58)	C ₁₁ (saturated)	294	78%
7-Substituted 8-Hydroxy- guinoline	TN 1911 (59)	C ₁₀₋₁₃ (unsatur- ated)	311	82%
	TN 2181 (59)	C ₁₀₋₁₃ (unsatur- ated)	311	81%
Tri-alkyl Phosphine Oxide	Cyanex 923 (60)	$n-C_6$ and $n-C_8$	348	938

Table 4.1: Summary of Extractant Characteristics







Where R is a 6 to 8 carbon chain

Figure 4.1: (a) 7-substituted 8-Hydroxyquinoline Derivatives (b) Tri-alkyl Phosphine Oxide In all cases, the extractants were diluted with Solvesso 150⁴ (a diluent with 97% aromatic content) and tridecanol (Harcros Chemicals) was added as a phase modifier. The relative percent composition of the various organic solutions used are as follows, (unless otherwise specified):

TN 1911, TN 2181 and Kelex 100: 2% extractant, 5% tridecanol and 93% Solvesso 150.

Cyanex 923: 0.6% extractant, 5% tridecanol and 94.4% Solvesso 150.

In all cases, this corresponds to approximately a 1×10^{-2} M extractant solution.

The organic solutions were not used directly as prepared, but rather, were subjected to a conditioning stage. This involved contacting the organic solution with an equal volume of approximately 3M HCl for three minutes to wash out all of the acid soluble organic compounds. The acidified organic phase was then subjected to four three-minute distilled water contacts at an aqueous to organic (A/O) ratio of 1.

The Rh aqueous solutions were prepared using $Na_3RhCl_6xH_2O$, either generously provided by Johnson Matthey Co (London, U.K.) or obtained from Aldrich Chemicals Co (Milwaukee, USA). All other reagents such as $MgCl_2$, $CaCl_2$, NaOH and various acids, were of reagent grade. Water deionized in a two-column Cole Parmer ion exchanger system was used for all of the aqueous solutions.

The solutions were made by weighing appropriate amounts of each of the required chemical and dissolving them in

ş

Proprietary product of Exxon Chemicals Co.

previously prepared HCl/H_2O solutions. For the experiments which required aged solutions, the aqueous solutions were left to rest at room temperature for the desired period of time.

4.2 Rh-Sn Feed Pretreatment

For the experiments involving the use of $SnCl_2$, the aqueous solutions were subjected to a pretreatment prior to contact with the organic solution. The solutions were prepared by dissolving appropriate amounts of $Na_3RhCl_6xH_2O$ and (usually) MgCl₂ in a HCl/H₂O solution. To this the required amount of a 0.5M SnCl₂ in 1.4M HCl solution was added. The Rh-Sn feed was then heated on a hot plate to about 70°C for fifteen to twenty minutes. A color change from red-pink to orange-pink to dark wine-red was observed as the solution was heated. The solution was then removed from the heat and allowed to cool to room temperature prior to contact with the organic phase.

4.3 Procedure

* ع

All of the tests were performed using 125-mL separatory funnels fixed to a Burrell automatic wrist action shaker (model 75). Prior to contact, a sample of the aqueous feed solution was taken for subsequent Rh content analysis. The aqueous and organic phase volumes were measured with a volumetric cylinder and unless otherwise indicated, the A/O ratio was 1 for all of the experiments. Due to the substantial value of Rh, the volume of solution was kept to a minimum and, in general, only 10 to 25 mL of each phase was used in the contact experiments. After contact and phase separation. samples of the raffinate were kept for Rh analysis. As well, acidity measurements of the raffinates were obtained either with a Fisher Accumet (model 810) pH meter using an ordinary pH electrode or through a standard acid-base titration. Titration were performed manually using NaOH and phenolphthalein as the end-point indicator.

4.4 Rh Concentration Determination

÷.

The Rh concentrations in the feeds and raffinates were determined with a 357 Instrumentation Laboratory atomic absorption spectrophotometer using standard techniques. All Rh samples were diluted to the linear region using 1.4M HCl and the standards were also prepared using 1.4M HCl and an Aldrich Rh standard. A drop of 100 g/L LaCl₃ was added to all samples and standards so as to minimize the effect of sodium and magnesium on the Rh determinations. As well, a nitrous oxide-acetylene flame was used rather than the more common air-acetylene flame, once again to minimize the effect of sodium and magnesium. For those experiments which involved the use of Sn, the Sn analyses were performed similarly to those of Rh. The wavelengths used for the Rh and Sn analyses were 343.8 and 235 nm, respectively.

The percent extraction was taken as the difference in Rh concentration between the feed and the raffinate by assuming no phase volume changes.

% Extraction = [Rh in feed] - [Rh in raffinate] x 100 4.1 [Rh in feed]

In some cases, the distribution coefficient, D, was calculated rather than the percent extraction. Distribution coefficients relate the amount of extracted metal in the organic phase to that left in the aqueous phase as follows:

$$D = [Rh in organic] 4.2$$
[Rh in aqueous]

<u>CHAPTER 5</u> Results and discussion

The research work presented and discussed in this chapter is divided into three parts. In part 1, the extraction behaviour of Rh(III) during the recovery of Pt(IV)/Pd(II) with 8hydroxyquinoline reagents (61) was investigated with the objective of defining conditions suppressing its C0extraction. In part 2, the behaviour of Rh(III) in modified 8-hydroxyquinoline systems was examined in the hope of formulating a process which could be used to quantitatively extract Rh(III). Finally, in part 3, the activation of Rh(III) as a mixed Rh-Sn chlorocomplex and its extraction with 8-hydroxyquinolines was investigated as a potential new recovery/purification method.

5.1 Rh EXTRACTION SUPPRESSION IN AN 8-HYDROXYQUINOLINE Pt/Pd SOLVENT EXTRACTION CIRCUIT

As shown in Figure 2.1, Rh is the last metal recovered in a precious metal refining flowsheet. It is thus important that Rh(III) not be coextracted during any of the preceding solvent extraction stages so as to avoid losses of the metal and contamination of the other PGMs. With reference to Pt/Pd solvent extraction, McGill University researchers (G.P Demopoulos (5,61-64), B. Côté-Ph.D. in progress (59), V. Aprahamian-M.Eng.(64)) have been involved in the development of a new solvent extraction process in which 8-hydroxy-quinoline reagents are used.

It is therefore important to study the behaviour of Rh in this particular Pt/Pd circuit so as to devise methods by which to suppress the extraction of Rh in that circuit such that no Rh losses will be incurred.

extractants presently advocated as the preferred The extractants in Pt/Pd solvent extraction are 7-alkylated 8hydroxyquinoline derivatives (R-HQ) such as TN 1911 (61) and TN 2181 (59). The principal difference between these two TN reagents is in the structure of the alkyl side-chain with TN 2181 having an overall lower steric hindrance (59). Because there is strong likelihood that one of the TN reagents may ultimately be industrially employed as an extractant for either Pt(IV) or both Pt(IV) and Pd(II), the behaviour of Rh(III) in this system is of prime importance. As important is the fact that by studying this system, knowledge is gained about the solution response of Rh(III) which may prove valuable in the subsequent work dealing with the design of a new solvent extraction method.

There are two main mechanisms by which Rh can be extracted by the R-HQ reagents; either through chelation or through ion-pair formation.

Chelation:
$$RhCl_6^{3-} + 3R-HQ \rightarrow Rh(R-Q)_3 + 6Cl^{-} + 3H^+$$
 5.1

Ion-pair formation:

Ś.

4

protonation of extractant: $R-HQ + HCl \rightarrow R-H_2Q^+Cl^{-5.2}$ extraction: $RhCl_6^{3-} + 3R-H_2Q^+Cl^{-} \rightarrow RhCl_6^{\bullet}(R-H_2Q)_3 + 3Cl^{-5.3}$

A number of different parameters affecting the extraction of Rh(III) with R-HQ were investigated and these included the effect of acidity, total chloride concentration, age of solution, temperature of aging, sulfate presence and concentration, contact time, extractant concentration and the addition of a second extractant to the organic phase.

Initial tests were performed on both TN reagents, namely TN 1911 and TN 2181 in order to determine if the behaviour of Rh would differ significantly depending on the extractant. The extractant which showed the highest affinity for Rh, TN 2181, was then retained for further experiments in order to consider the worst case scenario. Table 5.1 lists the tests which were performed on each of the different extractants.

Test	TN 1911	TN 2181
Feed Acidity (0.7 to 8M HCl)	x	X
Feed Acidity (pH 0.5 to 3.5)	х	
Reproducibility		X
4M Cl	X	X
Cl Concentration (0.7 to 4M)	X	
Aging (O to 7 days)	Х	x
Aging at 60°C (0 to 4 days)		X
SO ₄ ² Addition		X
SO_4^{2} Concentration (0 to 2M)		X
Contact Time (3 and 30 min)	X	

Table 5.1: Parameters Investigated with the TN extractants

Because the solutions were prepared using $Na_3RhCl_6.xH_2O$, the extraction was often tested for both freshly prepared solutions and solutions which were allowed to age 24-168 hours (1 to 7 days) since as discussed previously (Chapter 2.2.3), $RhCl_6^{3}$ undergoes aquation rather easily and the amount of $RhCl_6^{3}$ in a freshly prepared solution will decrease until it reaches equilibrium. By freshly prepared solutions, it is meant solutions which were not normally allowed to age for more than five to 10 minutes prior to contact with the organic.

Ív.

5.1.1 Effect of Feed Acidity in the High Acid Region (0.7 to 8M HCl)

Å.

į

The effect of the feed solution acidity on the amount of Rh(III) extraction was investigated in the region 0.7 to 8.2M HCl (about 25 g/L to 300 g/L). Figure 5.1 depicts the percent extraction of Rh as a function of HCl concentration in the raffinate for both TN extractants contacted with freshly prepared Rh feeds. The effect of the feed acidity was also tested for solutions which were allowed to age at room temperature for a period of three days and the results are presented in Figure 5.2. On the same figure, the theoretical abundance of the RhCl₆^{3.} (dashed line) is included as calculated previously (equation 3.14 and Figure 3.5). According to rate constants (equations 3.5, 3.7, and Appendix A) for the aquation/anation of RhCl₆^{3.}/RhCl₅(H₂O)², the feeds should have reached equilibrium after much less than three days.

For the results shown in the two figures mentioned above, it can be observed that, generally, for both a fresh and an aged solution, the percent Rh extracted increased with increasing acidity. This can be explained due to the fact that if the extraction mechanism is ion-pair formation, then an increase in acidity should help to increase the extraction degree since the extractant would become protonated more and more easily and extensively.

Protonation of extractant: $R-HQ + HC1 \rightarrow R-H_2Q^+C1^-$ 5.2

Another reason for the increase in extraction degree with increasing HCl concentration in the feed may be that the overall abundance of $RhCl_6^{3}$ increases due to the increase in total chloride ion concentration arising from the HCl. The following reaction, in other words, is expected to be shifted to the right.



Figure 5.1: Rh extraction from 0.7 to

600 ppm Rh feed, 10 min CT, A/O-1, 2 volume % extractant

Figure 5.2: Rh Extraction from 0.7 to 8.0 M HCl Feeds- 3 Day Aged Solutions



⁶⁰⁰ ppm Rh feed, 10 minCT, A/O-1

$$RhCl_{5}(H_{2}O)^{2} + Cl^{-} \rightarrow RhCl_{6}^{3} + H_{2}O$$
 5.4

*

Due to the substantial hydrophilicity of the aquated Rh-Cl complexes, it is presumed that the species extracted was $RhCl_6^{3-}$ and therefore, the degree of extraction depends very much on the abundance of this particular species in the feed solution. In fact, the percent Rh extracted followed quite closely the percent $RhCl_6^{3-}$ (dashed line in Figure 5.2) in solution except at high acidities where the extraction degree was lower than the expected abundance of $RhCl_6^{3-}$. Overall, this may be taken as an indication that the extracted species was indeed $RhCl_6^{3-}$.

The non-agreement between the abundance and the extraction degree of Rh at high acidities may be explained by considering the overall extraction equilibria/reactions.

$$RhCl_6^{3} \rightarrow RhCl_5(H_2O)^2 + Cl^2$$
 5.5

$$R-HQ + HC1 \rightarrow R-H_2Q^+C1^- 5.2$$

 $RhCl_{6}^{3-} + 3R-H_{2}Q^{+}Cl^{-} \rightarrow RhCl_{6}^{\bullet}(R-H_{2}Q)_{3} + 3Cl^{-}$ 5.3

It is possible that at acidity levels of 5.5 and 8.2M HCl (about 200 to 300 g/L HCl), the total chloride ion concentration is high enough to push reaction 5.5 to the left but to hinder the complete progression of reaction 5.3 due to the large number of chloride ions produced in the latter reaction.

Although no very great variation in percent extraction between the two extractants was observed, it can still be concluded that TN 2181 extracted marginally more Rh(III) than TN 1911. The slight superiority of TN 2181 over TN 1911 as an extractant for Rh may possibly be explained by the lower steric hindrance of TN 2181 and therefore, the greater ease of approaching three TN 2181 molecules around $RhCl_6^{3-}$ (see Figure 5.3).



Figure 5.3: Ion-Pair Formation Between TN and Hexachlororhodate

5.1.2 Reproducibility of Results

To determine the reproduciblity of the results, the Rh extraction test at 0.7 to 8.0M HCl with TN 2181 was performed twice; the tests being performed on different days and with different Rh feed solutions. Figure 5.4 depicts the results obtained. It was found that the trend was alike for both experiments but that variations occurred. In general, a difference of 5% in percent Rh extracted existed between the two trials and was therefore chosen as being representative of the experimental uncertainty for all Rh extraction results.





600 ppm Rh, TN 2181, 10 min CT, A/O-1

5.1.3 Effect of Contact Time

ĬĮ.

ł

One of the initial tests performed was the determination of the effect of contact time (CT) on the extraction of Rh and as shown in Figure 5.5, contact time did not have a large effect. Contact times of 3 and 30 minutes are compared and although deviations did occur, the percent extraction usually fell within the 5% experimental error determined in section 5.1.2. For this reason, a standard contact time of 10 minutes was used for the further experiments. This contact time was chosen because it is both a short period of time in which to run an experiment and because in light of Figure 5.5, it is clearly enough to reach "equilibrium" levels.





400 ppm Rh, TN 1911, 4M Cl, A/O-1

5.1.4 Effect of Addition of Cl salt in the Region 0.7 to 2.7M HCl

Industrial feed solutions contain significant amounts of chloride salts in addition to HCl. Thus, the effect of chloride ion concentration was investigated in a series of tests in which $MgCl_2$ was added to feed solutions of different acidities so as to ensure that the feeds contained a total of about 4M chloride ion (considering both $MgCl_2$ and HCl). The results obtained are shown in Figures 5.6 and 5.7 for a fresh and a three day aged solution, respectively. Overall, TN 2181 gives once more superior extraction levels.

At 4M chloride ion, using the speciation diagram presented previously (Figure 3.5), the abundance of $RhCl_6^{3-}$ at equilibrium should be about 32%. Assuming that all solutions contained chloride ion concentrations in the range of 3.5 to 4.5 M, then the $RhCl_6^{3-}$ abundance should vary from about 28 to 35%. This corresponds quite well to the percent extraction obtained for the 3 day aged solutions which should indeed have reached equilibrium.

Once again, it can generally be concluded that an increase in acidity increased the Rh extraction degree for both fresh and aged solutions even when the total chloride ion concentration was constant at about 4M. It is therefore clear that total chloride concentration is not the only parameter which governs the amount of Rh extracted but that the feed acidity is also important since for the ion-pair formation extraction mechanism, the acidity level is also of great importance. For example, the Rh extraction degree for an aged solution at 0.7M HCl was lower than the expected abundance of $RhCl_6^{3}$. It is possible that at this acidity level, the extractant was not protonated to a sufficiently high degree to completely extract all of the available $RhCl_6^{3}$.



Figure 5.6: Rh Extraction at [CI-] = 4M Fresh Solution

500 ppm Rh Feed, 10 min CT, A/O-1

Figure 5.7: Rh extraction at [CI-] = 4M 3 Day Aged Solutions



500 ppm Rh, 10 min CT, A/O-1

It is interesting to compare the extent of extraction when a chloride salt is added (to maintain about 4M chloride ion) with solutions having only the chloride level from HCl. Figure 5.8 shows the curves obtained for Rh extraction with TN 1911. As expected, the addition of a chloride salt to the Rh feeds has the effect of increasing the percent Rh extraction for both a fresh and an aged solution. The increase, which varied anywhere from about 10-20% was most likely due to the increase in the overall abundance of RhCl_b³-.

It is also quite evident that the increase was highest for the feeds at the lower acidity, 0.7 and 1.4M HCl. This is expected since these solutions contain little initial chloride ion compared to the 2.7M HCl feed and therefore the increase to 4M total chloride was significant.

The effect of the total chloride concentration was studied further by analyzing the degree of Rh extraction from solutions containing 0.7M HCl but different amounts of total chloride ion concentration achieved through the additions of MgCl₂ or CaCl₂. The results obtained for a three day aged feed are represented in Figure 5.9. Indeed, the total chloride ion concentration does seem to have a direct influence on the amount of Rh extracted. The extraction degree compares well with the theoretical RhCl₆^{3.} abundance as shown in Figure 5.9.

5.1.5 Rh Extraction in the Low Acid Region (pH = 0.5 to 3.5) It is clearly apparent from the results presented above that Rh(III) extraction (though limited to about 30-40%) tends to increase with both chloride ion concentration and acidity. To investigate further the effect of acidity, the extraction of Rh(III) was studied in the lower acid region (pH 0.5 to 3.5 when chloride ion concentration was kept constant at 4M).

Figure 5.8: Effect of Total [CI⁻] on Rh Extraction (Fresh and 3 Day Aged)

Ł



600 ppm Rh, TN 1911, 10 min CT, A/O=1

Figure 5.9: Rh Extraction at Various Total Chloride Ion Concentrations



400 ppm Rh, 0.7M HCl, CaCl2 or MgCl2, 10 min CT, TN 1911

As can be observed in Figure 5.10, the percent Rh extraction in the low acid region was suppressed when compared to that obtained in the 0.7-2.7M HCl region. Also, aging (even only one day) had a sharp effect on the amount of Rh extracted. In most cases, for a solution which had undergone aging, the percent Rh extracted was so low that it could be considered as nil since it fell within the experimental uncertainty.

The difference in extraction degree between the fresh and aged solutions may possibly be explained by the formation of other aquo-chlorocomplexes, such than simple as polynuclear complexes or even partially hydrolyzed species. The latter are known to be the dominant Rh(III) complexes pH > 2.9 (9) and it is thus possible that some amount is formed below this pH level. The formation of either hydrolysed or polynuclear species would have an effect on the abundance of both $RhCl_{6}^{3}$ and $RhCl_{5}(H_{2}O)^{2}$ and ultimately on the degree of extraction as shown in Figure 5.10.

As mentioned above, a solution which contains 4M chloride should contain about 30% $RhCl_6^{3-}$ and as the extraction was much lower than 30% (even for fresh solutions), it seems that in the very low acid region the degree of extraction is not limited by the amount of $RhCl_6^{3-}$ present but rather by the solution acidity which controls the protonation of the extractant.

$$R-HQ + HC1 \rightarrow R-H_2Q^+C1^- 5.2$$

Thus, assuming always that the extraction mechanism is ionpair formation, then the decrease in proton concentration leads to a decrease in extraction since it becomes more and more difficult for the extractant to protonate and become positively charged. The non-extraction of Rh from very low





400 ppm Rh, TN 1911, 15 min CT, A/O=1

acid feeds is another indication that the mechanism of extraction of $RhCl_6^{3}$ is ion-pair formation.

The results from Figures 5.6, 5.7 and 5.10 for TN 1911 were grouped in a single graph (Figure 5.11) by converting HCl concentrations to the pH scale. For estimating the proton activity of the HCl solutions, Jansz's methodology (Appendix B) was followed. The acidity effect is clearly obvious in this Figure as is the fact that aged solutions are not extracted to the same extent as fresh solutions.

5.1.6 Effect of Aging

It is expected that as solutions age, the extraction degree will drop until the solutions attain equilibrium due to the continuing aquation of $RhCl_6^{3-}$. It has already been shown that aging has a lowering effect on Rh extraction. This is further illustrated with Figure 5.12. This Figure is particularly interesting in that it shows both the aging and the acid effect. Clearly, the highest extraction was obtained for a fresh, very acid solution. Also, with aging, the extraction degree dropped slowly for the high acid solutions ([HCl] > 0.7M) but came to almost zero in the low acid region. Also, it is clear that there was very little change in extraction degree between the 3 and 7 day aged solutions which is as expected since by 3 days, the solutions should have reached equilibrium (Chapter 3).

During the industrial processing of the PGM solutions, the solutions are sometimes heated for a certain period of time. It is known that the temperature of the solution has a positive effect on Rh's rate of aquation (9). It is therefore expected that the abundance of $RhCl_6^{3}$ should be lowered with increasing temperature even though Figure 3.4 did not show this trend. A Rh solution was heated to 60°C and the
Figure 5.11: Rh Extraction at 4M Cl⁻ in the acid region 2.7M HCl to pH 3.5



400 ppm Rh, TN 1911, 15 min CT, A/O=1 H'activity calculated through Janz's method (appendix B) for 0.3 to 2.7M HCI feeds

Figure 5.12: Rh Extraction at Various Ages & HCI Concentrations - no extra Cl



500 ppm Rh, TN 1911 or 2181, 10 min CT

-

extraction degree was tested at various intervals once the samples had been allowed to cool to room temperature. The results obtained are shown in Figure 5.13. As expected, the extraction degree was lower for solutions which were heated prior to extraction. This is another indication that the Rh species which is extracted is probably $RhCl_6^{3}$.

5.1.7 Effect of the Presence of Sulfate

industrial solutions Because feed sometimes contain significant amounts of sulfate, it was important to determine if sulfate or bisulfate had any effect on the extraction of Rh. Aqueous solutions containing both 4M chloride and 1M sodium sulfate (Na_2SO_4) were prepared and the extraction results were compared to those obtained from solutions containing only 4M chloride. The results, presented in Figure 5.14, show that for both fresh and 3 day aged aqueous solutions, the percent extraction decreased significantly in the presence of sulfate. The trend of increased extraction with increasing acidity appeared to remain.

It was also deemed necessary to determine if the overall sulfate concentration had an effect on the percent extraction of Rh. Solutions of 0 to 2M sulfate at 1.4M HCl and 4M chloride were prepared and the extraction degree was determined. The results obtained for both fresh and aged solutions are shown in Figure 5.15. The results show that a concentration of 0.5M sulfate was enough to significantly suppress the extraction of Rh and that higher concentrations did not lead to a further decrease in overall extraction.

As the goal of this study was to suppress the extraction of Rh in the Pt/Pd circuit, the depression of Rh extraction in the presence of sulfate is considered important and beneficial.



3

;



400 ppm Rh, 1.4M HCl, 4M Cl, TN 2181, 10 min CT



Figure 5.14: Rh extraction at 4M Cl with or without 1M SO4

400 ppm Rh, TN 1911, 10 min CT, A/O-1

Figure 5.15 Effect of SO²⁻ on Rh Extraction



500 ppm Rh, TN 2181, 4M Cl, 10 min CT

5.1.8 Stripping Tests

A few stripping tests were carried out, not because the system holds any promise as an industrial extraction system for Rh but rather to try to get information about the possible extraction mechanism.

In general, when the extraction mechanism is chelation, then the stripping agent is a strong acid.

Extraction:
$$M^{n+} + nHL = ML_n + nH^+$$
5.6Stripping: $ML_n + nH^+ = M^{n+} + nHL$ 5.7

When the extraction mechanism is ion-pair formation, then the stripping agent is more likely to be water or slightly acidified water in order to avoid hydrolysis of metal ions transferred in the aqueous phase.

Extraction:
$$MX^{n-} + nR - H_2Q^+Cl^- \rightarrow MX(R - H_2Q)_n + nCl^-$$
 5.8
Stripping: $MX(R - H_2Q)_n + H_2O \rightarrow MX^{n-} + nR - HQ + nH^+ + H_2O$ 5.9

Two stripping solutions were tested, namely 0.14M and 0.33M HCl solutions. Both solutions gave good stripping results (about 90%) and this further indicates that the extraction mechanism is ion-pair formation.

5.1.9 Suppression of Rh in the Pt/Pd Solvent Extraction Circuit

Using all of these results, it should be possible to identify conditions under which Rh extraction will be suppressed in the Pt/Pd circuit. Ideally, in order not to lose any Rh, the feed solution should be at an acidity level of about pH=1, with as low a chloride ion concentration as possible. As well, the solution should contain some sulfate and any heating which it undergoes would be considered as beneficial. Realistically, however, these parameters are not feasible because the Pt(IV) and Pd(II) extraction would most likely suffer.

The extraction is in fact performed at about 1-2M HCl (61) and the total chloride concentration can vary but is more often in the range of 4M. Reducing the chloride concentration to much lower levels either through osmosis or through precipitation would not be economically justifiable. However, some relatively simple techniques could be used to favour the nonextraction of Rh.

The simplest technique would involve the addition of a sulfate salt to some level such that the Rh extraction would be significantly lowered and as determined previously (Figure 5.15), it is not necessary for a large amount of sulfate to be present to reduce the Rh extraction.

Another technique would involve aging the solution at a low pH (about 1.5) for 24 hours and then reacidifying it to the necessary level for Pt and Pd extraction. As long as the reacidification and extraction steps are performed very quickly, the Rh is not extracted to the same degree as it would be without a period of aging at low acidity. This approach was tested in the laboratory and an extraction degree of less than 10 percent was achieved. The two possible routes of suppressing Rh extraction in a Pt/Pd circuit are indicated in Figure 5.16.

It may, however, prove to be realistically impossible to completely inhibit the extraction of even small amounts of Rh under acidity (1 to 2.5M H⁺) and chloride concentration (4M) conditions which are necessary for the Pt/Pd circuit and which are also somewhat favourable for Rh's extraction.

Figure 5.16: Possible Rh Suppression Techniques for the R-HQ Pt/Pd Circuit



đ

5.2 Rh EXTRACTION IN MODIFIED 8-HYDROXYOUINOLINE SYSTEMS

The main aim of this work was, above and beyond trying to formulate procedures to suppress the extraction of Rh in the Pt/Pd 8-hydroxyquinoline extraction circuit, the development of an industrially acceptable solvent extraction system for Rh(III).

5.2.1 Synergistic 8-Hydroxyguinoline System of Rh(III)

Many experimental approaches were investigated and one of these dealt with an attempt to develop a synergistic system between R-HQ and a secondary extractant. The two secondary extractants tested were Cyanex 923 (Chapter 4.1) and Versatic Acid 10 (Chapter 4.1). The organic phases for the synergism experiments were composed of equal volumes of 1.3 $\times 10^{-2}$ M TN 2181 and either, (i) 1.3 $\times 10^{-2}$ M Versatic Acid 10, (ii) pure Versatic Acid 10, or (iii) 1.3 $\times 10^{-2}$ M Cyanex 923.

For the Versatic Acid 10 trials, aqueous feed solutions having acidities ranging from 0.3 to 5.5M HCl were tested and for Cyanex 923, only one acidity level of 0.3M HCl was tested. In all cases, the total chloride concentration was kept constant at about 4M total chloride through the use of MgCl₂. The results obtained for all systems studied revealed that the addition of the secondary extractant to R-HQ caused the overall extraction of Rh to significantly decrease rather than increase. The extraction degree obtained ranged from about 0 to 6% Rh extraction which is significantly lower than the Rh extraction obtained using TN 2181 alone (see Figure 5.1). The R-HQ-Cyanex and R-HQ-Versatic systems can actually be considered as antagonistic, rather than synergistic.

One possible explanation for this antagonistic behaviour may be that the two secondary extractants have a higher surface activity than does R-HQ. Surface activity is defined as the

an orientated monomolecular layer of at formation an interphase due to the strong adsorption of the molecule at the interphase (65) and therefore if the secondary extractants are more active, they will tend to occupy the interphase. It is natural for the extractants to be at the interphase since they have both a hydrophillic and a hydrophobic portion, and they will therefore tend to try to orientate themselves with the hydrophobic portion pointing into the bulk of the organic phase and the hydrophillic portion pointing towards the aqueous phase at the aqueous-organic interphase. It is this tendency which renders them surface active molecules and which also makes them somewhat similar to surfactants. It is known that in liquid-liquid systems, the addition of surface active molecules results in a lowering of the liquid phase masstransfer coefficient due to a suppression of large scale fluid motion in the interphase (surface stagnation) (66). Since the extraction of $RhCl_6^3$ with R-HQ must at some point include an interphase transfer of the Rh from the aqueous into the organic, then it follows that if the secondary reagents are more surface active than R-HQ, the transfer of Rh will be reduced both because R-HQ can no longer occupy the interphase and because the motion at the interphase is severely reduced (see Figure 5.17).

¥,

Í

Another possible explanation for the decreases in extraction which has been put forward (67) is that the addition of a secondary extractant in the organic solution causes the overall hydrogen bonding of the first organic extractant, in this case R-HQ, to increase. Since the extraction mechanism between R-HQ and $RhCl_6^{3}$ is expected to be ion-pair formation, then the formation of hydrogen bonding between the secondary extractant and R-HQ reduces the ability of R-HQ to form an ion-pair with HCl (equation 5.2) and therefore, reduces its ability to extract $RhCl_6^{3}$. Although theoretically the addition



(b) 8-Hydroxyquinoline and Carboxylic Acid Extractant

.

Figure 5.17: Schematic of Aqueous/Organic Interfaces

of a secondary extractant to R-HQ could be used to suppress the extraction of Rh(III) in the Pt/Pd circuit, it is probable that the presence of the secondary extractant would also suppress the extraction of Pt and/or Pd.

5.2.2 Extraction of Rh(III) by Intermittent Reequilibration of Aqueous Feed

Another approach which was investigated in order to achieve the extraction of Rh(III) with 8-hydroxyquinoline involved the assumption that under conditions of 1.4M HCl and 4M total chloride, all of the $RhCl_{6}^{3}$ available is extracted (Figure After phase separation, the raffinate should contain 5.6). almost only $RhCl_{4}(H_{2}O)^{2}$. It therefore follows that the aqueous solution will once again try to reach equilibrium to obtain a balance of about 70.30 $RhCl_{5}(H_{2}O)^{2}/RhCl_{6}^{3}$. As described previously, the anation of $RhCl_{5}(H_{2}O)^{2}$ is much slower than the aquation of RhCl³, however, it does nonetheless occur (about thirty minutes to reach equilibrium, see Appendix A). It was believed that if an aqueous Rh feed was contacted with R-HQ, allowed stand thirty the raffinate to minutes to reequilibrate, and the raffinate then recontacted with R-HQ, after a contact/reequilibration series of 3-4 times a significant amount of Rh could be extracted with R-HQ.

Two different tests were performed to investigate this possibility. The difference between the two tests is that in the first test, the same organic was used for every contact with the aqueous phase. In the second test, "fresh" organic was used for each contact, however, in both cases a total of four contacts were performed. Some very interesting results were obtained and are presented in Table 5.2. It was found for the first test that the extraction degree was 24% after the first contact and even after four consecutive contacts it never increased even though, after equilibration, "new" RhCl₆³⁻

was supposed to be available for extraction (Appendix A). For the system which used fresh organic for every contact, the overall extraction degree increased after every contact. In fact, approximately 24% extraction was observed for every contact to reach a total of about 66% initial Rh extracted after the four contacts that were tested. In other words, the distribution coefficient for Rh under the conditions of 1.4M HCl and 4M chloride was always respected since the extraction achieved at each contact was always about 24 \pm 2%.

Contact	"Same" Organic % Rh Extracted		"New" Organic % Rh Extracted	
	each contact	cumulative	each contact	cumulative
1	24	24	23	23
2	0	24	23	40.7
3	0	24	24	54.9
4	Û	24	26	66.6

Table 5.2: Experimental Results of Reequilibration Test

Somehow, it would seem that the organic becomes inactive after the initial extraction and then even if more $RhCl_6^{3}$ becomes available, the extraction does not progress.

As previously discussed, the extraction of Rh(III) by R-HQ is postulated to occur via ion-pair formation (equation 5.3)

 $RhCl_{6}^{3} + 3 R-H_{2}Q^{+}Cl^{-} \rightarrow RhCl_{6}(R-H_{2}Q)_{3} + 3Cl^{-}$ (5.3)

Under the conditions tested, 24% extraction of Rh represents only about 1/10 of the molar concentration of R-HQ. In other words, large excesses of the extractant are present which are supposed to extract the newly formed (after-reequilibration) RhCl₆^{3.}. Since this was not the case, it may be possible that upon extraction, $RhCl_6^{3}$ undergoes some type of complex transformation of unknown nature which somehow involves the molecules of R-HQ and which are thus rendered inactive. Another possible cause might be of interfacial nature. $RhCl_6 (H_2Q)_3$ may flocculate at the organic/aqueous interface due to its amphoteric and strong hydrophillic character. If the interphase is "filled" with Rh-(R-HQ), then it is no longer possible for the free organic in the bulk of the organic phase to reach the "new" $RhCl_6^{3}$ in the aqueous phase.

5.3 Rh EXTRACTION IN THE Rh-Sn-Cl/8-HYDROXYOUINOLINE SYSTEM.

Since the investigation on direct extraction of Rh(III) gave unsatisfactory results from the standpoint of identifying and designing a new separation process, it was decided to exploit another avenue; that of modification of the aqueous chloride speciation of Rh(III). As has already been reported in Chapter 2, investigators in the past have changed the matrix of the feed solution in several drastic processing procedures. These include evaporation to dryness and redissolution in chloride or pure water media to obtain either the fresh active $RhCl_{6}^{3}$ or to produce cationic Rh(III) species, treatments with NaNO₂ to obtain $Rh(NO_3)_6^3$ species as is done in the classical refining process, or even, forming other complexes such as RhSCN^x. All these techniques, however, were thought not to be practical or attractive from an industrial process point of However, the use of Sn(II) additions to labilize the view. PGM-chlorocomplexes, as has been reported in analytical chemistry literature, seemed more acceptable and it was explored in the present work.

5.3.1 Effect of Feed Acidity in the Acid Region 0.7 to 8M HCl

A series of Rh(III) aqueous solutions containing about 400 ppm $(4\times10^{-3} \text{ M})$ Rh and ranging in acidity from 0.7 to 8.2M HCl were treated with 0.05M SnCl₂ (as described in Chapter 4.2) and the extraction degree of Rh with R-HQ was determined. The results, presented in Figure 5.18, show very strong extraction of Rh independent of the HCl concentration in the feed. Replotting the same data in the form of distribution coefficient (D) versus HCl concentration (Figure 5.19) shows very high distribution coefficient values exceeding 100 for the fresh solutions.



2 vol% TN2181, .05M Sn, A/O+1, 10 min CT

No.

1

Figure 5.19: Rh Extraction with SnCl₂ and TN2181



2 vol% TN2181, .05M Sn, A/O-1, 10 min CT

Comparison of the results for a fresh solution versus a 3 day aged solution show that the effect of aging is negligible. The small decrease in extraction degree (about 2%) observed is more likely due to the aqueous feed solution preparation than to a real decrease in extractability. This is because, from visual observation, it seems that the degree of completion of the reaction between Rh(III) and Sn(II) is dependant on temperature and on the overall time of reaction. It is possible that the solution was not heated or allowed to react for a long enough period of time and therefore, the Rh(III) was not completely converted to the extractable form.

Aging in this system is not as important as in the Sn-free system because apparently all of the Rh-Cl complexes undergo a reaction with Sn(II). Thus the relative amount of RhCl³, in the feed solution is no longer important in determining the percentage of Rh extracted.

Having succeeded in quantitatively extracting Rh in the Rh-Sn-Cl system with TN 2181, Kelex 100 was also investigated as a potential extractant as both are members of the same 7alkylated 8-hydroxyquinoline derivatives family. The advantage in using Kelex 100 over TN 2181 is that Kelex 100 has a saturated carbon side chain and it is therefore more resistant/stable to concentrated HCl solutions. Two acidity levels were investigated, namely 1.4 and 5.5M HCl. Similarly to the TN 2181 results, the extraction degree was very high at both acidity levels as shown in Figure 5.20.

The effect of chloride ion addition on the extraction of Rh from the Rh-Sn-Cl system was also investigated with both reagents (TN 2181 and Kelex 100) at 1.4M HCl. In all of these tests, the total chloride concentration was maintained at about 4M (i.e., 1.4M coming from HCl and 2.6M from MgCl₂) in

76

order to ascertain that the presence of extra chloride would not inhibit either the Rh-Sn reaction or the extraction from occurring. Once again, the extraction degree was very high for both organic extractants. (see data points on Figure 5.20).

Figure 5.20: Rh Extraction with SnCl₂ and either Kelex 100 or TN 2181



0.05M Sn TN and Kelex A/O-1, 10 min CT, 250 ppm Rh in feed

It is noteworthy to observe that in the parallel Cyanex 923 system investigation (see Appendix D), increasing chloride ion and HCl concentrations were found to have a suppressing effect on Rh extraction from the Sn-activated chloride feed. Considering that in actual PGM refining solutions, high chloride ion concentrations are present this makes the 8hydroxyquinoline system quite attractive and powerful.

5.3.2 Sn Co-Extraction

Ideally, it would be preferable if the Sn which is added to the aqueous feed to render the Rh more "reactive" was not or was very slightly co-extracted with the Rh. In practice, this is not the case as 8-hydroxyquinolines are very good extractants for both Sn(II) and Sn(IV) (64,68). In general, the extraction degree of Sn(II) using either TN 2181 or Kelex 100 ranged from 65 to 80% extraction. Since the amount of Sn in the feed was much higher than that of Rh (generally, 5×10^{-2} M Sn versus 4×10^{-3} M Rh), the Sn in the organic represents a large excess over the Rh. Whether Sn(II) is extracted as part of a Rh-Sn complex or independently via a parallel competitive mechanism is addressed in Chapters 5.3.4 and 5.3.7.

5.3.3 Stripping of Rh from Loaded 8-Hydroxyguinoline

Having determined that it is possible to extract Rh by the addition of Sn(II) from this type of aqueous solution, it was then important to devise a technique by which to strip the Rh from the loaded organic. A number of different stripping reagents were tested and these are listed in Table 5.3 along with an average value of the stripping results obtained.

It is apparent that the only stripping reagent which gave satisfactory results was H_2SO_4 and this only in the case of Kelex 100. Thus H_2SO_4 and Kelex 100 were retained and further stripping experiments were carried out with an aqueous feed composed of 4M total chloride, 0.05M Sn(II), 1.4M HCl and about 400 ppm Rh. The effect of the H_2SO_4 concentration on the stripping capacity was studied using three different H_2SO_4 concentrations, 1.1, 1.7 and 2.3M. The results obtained are shown in Figure 5.21. After five five-minute contacts, the total percent Rh stripped was virtually equivalent for all three solutions, however, in most cases, it would seem that 4 contacts were sufficient to reach the maximum Rh stripped which ranged between 65 and 75%. Table 5.3: Summary of Exploratory Stripping Tests (Loaded 2 volume percent organic with aqueous feed of 400 ppm Rh $(4\times10^{-3}$ M), 4M Cl⁻, 0.05M Sn²⁺ at 1.4M HCl)

STRIPPING AGENT	PERCENT STRIPPING		
	TN 2181	KELEX 100	
Salts			
0.5M FeCl3	5		
0.2M Fe2(SO4)3	0		
0.4M NH4C1	0		
2M MgSO4 (pH 0.6)		0	
Acids			
8.2M HC1		0	
5.6M HNO ₃ (1 contact) (3 contacts)	17 20	16	
1.7M HNO3 (5 contacts)		0	
3.0M H_2SO_4 (2 contacts)		35	
1.7M (3 contacts)		74 71	
$1.7M + 1M SO_4^2$	14	85-100	
		77	
1.1M (5 contacts)		80	
2.3M (5 contacts)			
Special			
1M Tartaric acid	5		
0.05M EDTA	0		
Water	3rd phase formation/ precipitation	3rd phase formation/ precipitation	



2 vol% Kelex 100, A/O=1, 5 min CT, about 350 ppm Rh in loaded organic

It is also interesting to observe that after the first contact, there was no stripping of Rh, even for the $2.3M H_2SO_4$ solution. The reason for this may have to do with the residual chloride which is co-extracted as part of the Rh-Kelex complex. The first H_2SO_4 contact may actually serve as a chloride wash by replacing the chloride in the organic with either bisulfate or sulfate. Only when the chloride was no longer present did the stripping occur at which point, it is believed that some new type of Rh-SO₄ complex formed which was not extractable.

To try to determine whether protons (H^+) or sulfate $(SO_4^{2^\circ})$ alone could also strip the loaded organic, strip solutions imitating either the acidity or the sulfate level of the 1.7M H_2SO_4 strip solutions were tested. A 1.7M HNO₃ solution was tested and it was determined that even after five contacts, no stripping was achieved. It therefore appeared probable that the important functionality in the stripping reaction with H_2SO_4 is the sulfate group. A solution of 2M MgSO₄ at pH 0.6 was therefore tested as a possible strip solution for the Rhloaded R-HQ. Surprisingly, this solution also proved incapable of stripping the loaded organic. Therefore, it seems that it is the combination of both H⁺ and SO₄^{2.} that stripped the Rh from the loaded organic. Whether or not it is the HSO₄- ion which plays a role in this stripping mechanism remains to be investigated at a later stage (Ph.D. thesis work).

Although the H_2SO_4 stripping was better than all the other reagents tested, 75% stripping is not sufficient to consider the stripping media as being truly effective. Because the sulfate or bisulfate group may be more important than the proton in the stripping reaction, the addition of a sulfate salt to the 1.7M H_2SO_4 strip solution was also tested. A 1.7M $H_{2}SO_{4}$ + 1M Na₂SO4 solution was prepared and the degree of Rh stripping with this solution was tested. The results obtained are presented in Figure 5.22. In fact, the stripping degree was significantly higher at about 90% compared to the original 75%. Also, it can be considered to have been complete after 3-4 contacts.

The effect of contact time on the stripping efficacity of 1.7M $H_2SO_4 + 1M SO_4$ was also tested on the second strip contact for contact times ranging from 3 to 60 minutes. As depicted in Figure 5.23, the contact time did seem to have an effect, with the stripping degree increasing gradually through the first twenty minutes and then essentially levelling off. The contact time for the stripping tests performed for the other tests was set to five minutes and it is therefore possible that the total number of stages for the complete removal of Rh



2 vol% Kelex, A/O=1, 5 min CT, about 375 ppm in loaded organic

1

Figure 5.23: Contact Time Effect on Rh Stripping - 2nd 1.7M H₂SO₄ Contact



could be lowered from 4 to 3 if the contact time were increased to at least 15 minutes.

5.3.4 Stripping of Sn from Loaded 8-Hydroxyguinoline

Because Sn is coextracted with Rh, it is important to study its behaviour in the stripping stage. The amount of Sn stripped with either 1.7M H_2SO_4 or 1.7M H_2SO_4 + 1M $SO_4^{2^2}$ is shown in Figure 5.24. Here also, the amount of Sn stripped was slightly higher for the solution containing more total $SO_4^{2^2}$.

In fact, the amount of Sn stripped was correlated to the amount of Rh stripped as shown in Figure 5.25. In this Figure, the percent stripping data of Figures 5.22 and 5.24 have been replotted in terms of number of moles stripped for each metal. It is clear that there is a direct relationship between Sn and Rh stripping where 2 moles of Sn were stripped for every mole of Rh. This leads to the supposition that there is a mixed Sn-Rh complex having 2 coordinated Sn atoms per Rh atom which was stripped from the organic phase and it may therefore also be possible that a 2:1 Sn:Rh complex was the type which was extracted in the organic phase. Apparently the excess Sn in the organic was simply extracted as "free" Sn, and this was not stripped with H_2SO_4 . Aprahamian, who studied the extraction of impurities (including Sn(IV) and Sn(II)) in the 8-hydroxyquinoline system has indeed found Sn to be tenaciously held in the organic phase and not to respond to acid stripping (either strong HCl or strong H_2SO_4) (68).

To further substantiate the above, i.e. that the Sn which is stripped is indeed due to a Rh-Sn interaction and is not simply due to the normal Sn distribution in the 1.7M $H_2SO_4/Kelex$ 100 system, the extraction and stripping characteristics of Sn(II) and Sn(IV) were studied under the same conditions used for the Rh-Sn-Cl tests but this time in





Figure 5.25: Moles of Sn Stripped vs Moles of Rh Stripped



Ŕ

the absence of Rh. In fact, as expected, the extraction was complete and quantitative for both Sn states but the stripping with $1.7M H_2SO_4 + 1M Na_2SO_4$ was nil even after five contacts.

As only about 25-30% of the loaded Sn is stripped with the 1.7M H_2SO_4 + 1M Na_2SO_4 solution, it is important to devise a technique by which to strip the excess Sn out of the loaded organic. This was accomplished by adopting a caustic strip solution (1M NaOH) as has been determined by Aprahamian (68). This 1M NaOH solution was found to strip > 90% Sn(IV) and about 65% Sn(II) in two five-minute contacts. However, >90% Sn(II) stripping can be achieved in a single 1M NaOH contact if the contact time is sufficiently long (1 hour).

Because 1M NaOH is a suitable reagent to strip Sn, it was hoped that it would be possible to selectively strip the Sn before the Rh by contacting the loaded organic with two five minute contacts of 1M NaOH to remove the Sn. The Rh could then be stripped with the usual H_230_4/Na_2S0_4 strip solution. This approach, however, proved unsuccessful, and when this test was performed, it was found that the NaOH contacts somehow transformed the Rh-Sn-loaded organic in such a way that the consequent stripping of Rh with the H_2S0_4/Na_2S0_4 medium was no longer possible. The Rh had become "immune" to the H_2S0_4/Na_2S0_4 contacts once the loaded Kelex had been in contact with NaOH (see Figure 5-26).

Figure 5-26: Effect of the Stripping Order of H₂SO₄ and NaOH on Rh Stripping % Rh Stripped 100 80 60 40 20 0 5 6 7 2 3 8 0 1 Number of Contacts - NaOH/H,SO, --- H,SO,/NaOH

2% Kelex, A/O=1, 5 min CT, about 325 ppm Rh and 5000 ppm Sn in organic 2 NaOH(1M) and 6 SO4(1.7+1M) contacts

5.3.5 _Effect of Recycled Organic on Loading and Stripping The observed effect that the NaOH strip stages had on the subsequent stripping of the Rh-Sn complex with H,SO₄/Na,SO₄ (Figure 5-26) raised the alarming question if upon recycling (i.e., after a two stage H_2SO_4/Na_2SO_4 and NaOH stripping) the solvent would lose either its extraction capacity or strippability. A recycle test was thus performed in which after loading, the organic was stripped of Rh first with H_2SO_4/Na_2SO_4 followed by Sn with NaOH and was then washed (as explained below), reloaded and restripped. The results obtained are shown in Table 5.4. In fact, the extraction was complete for Rh for both loading stages and the two H₂SO₄/Na₂SO₄ stripping stages yielded the usual Rh stripping results. It appears therefore that as long as the Rh-Sn complex is stripped from the organic phase first with the H₂SO₄/Na₂SO₄

medium no undesirable complications with the performance of the solvent results. It is also probable that the organic wash with one three minute contact of 2.7M HCl, followed by two three minute contacts with slightly acidified H_2O , are necessary to render the organic effective after every cycle.

Table 5.4: Extraction and Stripping Results for Rh and Sn Using Recycled 2 volume percent Kelex 100 (Feed of 400 ppm Rh (about $4x10^{-3}M$), 4M Cl⁻, 1.7M HCl and 0.05M Sn²⁺)

Stage	<pre>% Rh Extracted or Stripped</pre>	<pre>% Sn Extracted or Stripped</pre>
1st Loading	100	85
1st 1.7M H ₂ SO ₄ + 1M Næ ₂ SO ₄ Stripping	0	0
2nd strip	56	9
3rd strip	86	12
4th strip	98	12
5th strip	99	12
1st 1M NaOH Stripping	100	50
2nd strip	/	58
2.7M HCl wash	/	/
1st H ₂ O wash	1	1
2nd H ₂ 0 wash	1	/
2nd Loading	100	72
2nd 1.7M H_2 SO ₄ + 1M Na ₂ SO ₄ Stripping	1	/
2nd strip	43	9
3rd strip	73	15
4th strip	81	16
5th strip	83	17

5.3.6 Comparison of Stripping Characteristics of TN 2181 and Kelex 100

As the results of Table 5.3 showed, Kelex 100 proved to be a better extractant than TN 2181 for the Rh-Sn-Cl system when stripping performance is considered. This was surprising as both reagents are 7-alkylated 8-hydroxyquinoline derivatives. Thus it was decided to conduct some further stripping tests to substantiate this trend. The results obtained are shown in Figure 5.27. As was initially noted, the stripping of Rh from the loaded TN 2181 could not be achieved with the H_2SO_4/Na_2SO_4 strip solution. The total amount of Rh stripped after 5 contacts was determined in three separate trials to be only between 0 and 15%. However, even in this case (i.e. TN 2181) Sn was found to be stripped at the same molar ratio of 2:1 Sn:Rh as in the case of Kelex 100.

Figure 5.27: Comparison of TN 2181 and Kelex 100 Rh Strippability



2 volume% extractant, 5 min CT, A/O=1,300 ppm Rh & 4500 ppm Sn in organic 1.7M H₂SO₄+ 1M Na₂SO₄strip solution

It is difficult to clearly explain the large difference in stripping behaviour between TN 2181 and Kelex 100. It is possible that the complexes formed with TN 2181 are stronger than those with Kelex for both electronic and steric reasons.

As mentioned previously, Kelex 100 and TN 2181 are both 7substituted 8-hydroxyquinoline reagents. The substituent R group in Kelex 100 is a saturated C_{μ} chain with a branched oriented towards the -OH and -N: active sites (58). However that of TN 2181 is unsaturated with its branch oriented away from the -OH and -N: sites (59). This difference in the composition and structure of the R group might be held responsible for the observed behaviour. In general terms, it may be thought that since Kelex 100 is more sterically hindered than TN 2181, the bond between Kelex and the inorganic extracted complex may be weaker than that of TN 2181. Also it is probable that the presence of double bonds in the alkyl side-chain changes the strength of the -OH and -N: active sites due to a change in the electron density of these sites.

5.3.7 Effect of Sn:Rh Molar Ratio

The extraction and stripping tests described above were carried out with about 400 ppm Rh(III) $(4\times10^{-3}M)$ and 0.05M Sn(II). Industrially, the addition of such a level of Sn(II) may not be considered advantageous, especially since the Sn is quite extensively loaded in the organic along with the Rh. The Sn:Rh ratio was therefore investigated with the intention of lowering it to a more acceptable level. From the stripping results, it was apparent that the Sn:Rh ratio in the strip solutions was 2:1 and therefore, it is reasonable to assume that 2 moles of Sn are extracted and stripped along with every mole of Rh. The Sn:Rh molar ratio was therefore studied from about 15:1 to 1:1. Figure 5.28 shows the results obtained to achieve complete Rh extraction and as expected, a molar Sn:Rh ratio of 2:1 is both necessary and sufficient to achieve this. Although the region 6:1 to 15:1 Sn:Rh is not shown in Figure 5.28, the Rh extraction remained complete in this region also.

Figure 5.28: Rh Extraction Dependance on the Sn:Rh Molar Ratio in the Feed



Feeds: about 400 ppm Rh, 4M Cl, 1.7M HCl

It was decided next to subject the 2:1 Sn:Rh loaded organic $(1\times10^{-2} \text{ M Kelex 100})$ to stripping using the usual 1.7M H₂SO₄/1M Na₂SO₄ medium. Surprisingly, the results showed that the Rh was no longer strippable (less than 10% stripping was obtained). Although at a 2:1 molar ratio of Sn:Rh there is enough Sn(II) to allow for complete Rh extraction (Figure 5.28), it seems that the complex extracted is such that it cannot be stripped with this medium. The Sn:Rh molar ratio is therefore obviously of prime importance in determining the amount of Rh extracted and stripped.

A number of Sn:Rh ratios were tested to determine the minimum Sn level with which Rh can be quantitatively stripped with the usual stripping medium and five five-minute contacts. The results are shown in Figure 5.29.

Figure 5.29: Rh Stripping Dependance on the Sn:Rh Molar Ratio in the Loaded Organic



² vol% Kelex, A/O+1,5 min strip contacts

There is a substantial amount of scattering in the results presented in Figure 5.29. The optimization of the necessary Sn:Rh molar ratio should therefore be further studied as the present results can only suggest that a molar ratio of about 12:1 is required to achieve, first, quantitative extraction and then, significant stripping. The 12:1 molar Sn:Rh ratio appears to be a little high since in order to get complete SnCl₃ complexation with Rh, only 6 moles of Sn are required per mole of Rh (12) and it is therefore difficult to explain the role of the "extra" 6 moles of Sn which seem to be required. The necessity for such an excess amount of Sn is even more difficult to explain in light of the fact that the Sn:Rh molar ratio in the Rh strip solutions is only 2:1 and that the "extra" 10 moles of Sn must then be stripped independently with 1M NaOH.

5.3.8 Discussion of Extraction - Stripping Mechanism

In terms of the extraction mechanism, it is clearly obvious from Figure 5.28 that to achieve complete Rh extraction, at least 2 moles of Sn(II) for every mole of Rh must be supplied in the feed. It is interesting to note that one of the Rh-Sn-Cl species which was originally proposed in the analytical chemistry literature is $[Rh_2Cl_2(SnCl_3)_4]^4$ (9, 18, 69) and indeed, in this complex, the Sn:Rh molar ratio is 2:1. The bridged Rh dimer was identified through precipitation with a large cation ((CH_1)₄N⁺) and subsequent chemical atomic analysis (69). The existence of this dimer was also supported by a far I.R.study (18). Although more recent studies (12) have not been able to identify this species in aqueous solutions, it may still be possible that this type of Rh dimer can be formed under certain conditions. It may then be extracted in the organic either directly from the aqueous solution or after some kind of complex transformation in the organic phase.

One main drawback to this explanation is that the addition of two moles of Sn(II) per mole of Rh(III) in the feed (as required for complete extraction) is not sufficient to both reduce Rh(III) to Rh(I) and to complex the Rh as in the dimer proposed above. Clearly, more direct analyses such as, possibly, UV analysis must be performed on the feed and on the loaded organic if the characteristics of the extracted complex are to be clearly determined.

The extraction mechanism is also difficult to clearly

determine from the results obtained for a number of reasons. First, the extraction can be considered as virtually quantitative from 0.7 to 8M HCl and no acidity effect was found (Figure 5-18). If the extraction mechanism is ion-pair formation, then usually the feed acidity has an effect since the protonation of the organic (equation 5.2) is more extensive as the acidity increases. In this system, however, it is possible that 0.7M HCl is sufficient to fully protonate the extractant and if this is indeed the case, then increasing the acidity to higher levels will not have any effect. In fact, in the work performed on the Sn free Rh/R-HQ system, it was believed that in the region 0.7 to 8M HCl, the limiting factor in Rh extraction was the abundance of RhCl₄³ and not the Since the Rh-Sn-Cl/R-HQ system protonation of the organic. was not studied in the pH region (as was the Sn free system), is not possible to conclusively determine that the it mechanism is ion-pair formation.

If the mechanism is chelation, then here also, the acidity should not have a strong effect except possibly at very high acidities were the -OH group could have trouble losing the H^+ for the O⁻ to coordinate with the inorganic complex. In most chelation type reactions, however, the metal is extracted alone (no coordinated ligands) and it would then be difficult to explain the stripping of 2 moles of Sn per mole of Rh in the strip solutions.

The extraction mechanism is also often determined from the type of stripping media which are found to be effective. In general, for ion-pair formation mechanisms, the stripping medium is water (to break apart the ion-pair) and in chelation, it is a strong acid (to reprotonate the hydroxyl group and break apart the 0'/metal bond). In this case since the effective medium is a relatively strong (1.7M) H_2SO_4

solution, it would be simple to label the mechanism as chelation, however, it should be remembered that other much stronger acids such as 5.6M HNO₃ and 8.2M HCl were not effective as stripping agents. It is also impossible to directly label the mechanism as ion-pair formation since a solution of 2M MgSO₄ at pH 0.6 also proved to be ineffective as a stripping media. Nonetheless, an ion-pair formation mechanism seems more reasonable than chelation due to the supposition of some type of Rh-Sn complex in the organic phase. In effect, however, the mechanism cannot be positively determined from the results obtained to date and more work must be performed before this is known.

As for the stripping reactions, there are two possible reasons to explain the drop in stripping ease as the Sn:Rh molar ratio in the loaded organic decreases (Figure 5-29). It has been reported that as the number of $SnCl_3$ ligands increases, the bond strength of the Rh-SnCl₃ bonds decrease (12). So, when there is only a 2:1 Sn:Rh molar ratio, it is possible that the bonds between Rh-SnCl₃ and Rh-Cl are too strong for $SO_4^{2^2}/HSO_4^{-1}$ to break them apart (if these two sulfate species are indeed those responsible for the stripping of the loaded Rh).

The second reason may have to do with the actual species which form between Rh and Sn. As explained previously, in order for all of the chloride ligands to be replaced by SnCl₃ ligands, the Sn:Rh ratio must be at least 6:1. Although a ratio of 2:1 may be enough to render the Rh "reactive" enough to extract it, it is likely that the Rh complex still contains 4 chloride ligands and, as well, that the Rh is still in the +III oxidation state, (according to the most recent Rh-Sn(II) studies (12)). It is possible that this octahedral Rh-Cl-Sn complex is unstrippable although it is completely extractable.

By raising the Sn:Rh ratio to 6:1 and higher, the Rh complex becomes $[Rh(SnCl_3)_5]^4$ (12) and this species may be the one which is indeed strippable since this complex has a reactive Rh(I) species, is not octahedral and has a very high charge.

The first H_2SO_4/Na_2SO_4 strip solution may therefore serve to remove the chloride ion from $R-H_2Q^+Cl^-$ (equation 5.2) to possibly convert it to $R-H_2Q^+(HSO_4^-)$ and allow the formation of some new type of $Rh-Sn-SO_4$ complex where the molar ratio of Sn:Rh in this complex is 2:1.

It is clear that a number of properties or characteristics of this Rh-Sn-Cl/R-HQ system remain either unclear or unknown and some of these will be addressed in the Ph.D. work which is to follow. It must not, however, be overlooked that some major aspects of this system have been discovered and these have been assembled to propose a preliminary flowsheet for the industrial application of this system (see Figure 5-30).


Figure 5.30: Proposed Preliminary Flowsheet for the Recovery of Rh using 7-alkylated 8-Hydroxyquinolines

ĺ

<u>CHAPTER 6</u> <u>CONCLUBIONS</u>

6.1 Speciation

It is clear that there are only limited data available describing the thermodynamics of Rh in aqueous chloride solutions. Nevertheless, an estimation of the speciation of Rh in chloride solutions such as those in PGM refining has been performed using kinetic-based stability constants. The speciation diagram constructed (Figure 3.5) has been found to be in good agreement with some subsequent experimental extraction results. It is therefore believed that this limited speciation diagram represents more closely the relative abundance of the various anionic chloro-species of Rh than do the previously published speciation diagrams.

6.2 Rh Extraction Suppression in an 8-Hydroxyquinoline Solvent Extraction Circuit

The extraction of Rh in acidic chloride solutions follows quite closely the calculated abundance of hexachlororhodate. The extraction degree has been found to be directly proportional to acidity and chloride ion concentration, and inversely proportional to age and temperature. The mechanism of extraction is likely ion-pair formation. In terms of suppressing the extraction of Rh with 8-hydroxyquinoline derivatives from chloride solutions, the addition or initial presence of sulfate helps to significantly reduce the extraction degree of Rh. As well, it was found that aging Rh solutions at low acidity (pH 1.5) for one day helps to reduce the extraction degree even if the solutions are reacidified prior to contact with the organic extractant. However, a procedure to completely inhibit the extraction of Rh from acidic chloride solutions was not found and some extraction (about 10%) can be expected to occur even in the presence of sulfate.

6.3 Extraction of Rh from Rh-Sn-Cl Aqueous Solutions with 8-Hydroxyquinolines

Rh can be quantitatively extracted with 7-alkylated 8hydroxyquinoline derivatives from aqueous chloride solutions when these are pretreated with a sufficient quantity of $SnCl_2$. For complete extraction, the Sn to Rh molar ratio must be at least 2:1. It appears that some of the Sn is co-extracted with the Rh as part of a Rh-Sn complex and that any excess Sn (not part of a Rh-Sn complex) is also co-extracted as an impurity. A single ten-minute contact was sufficient to quantitatively transfer the Rh from the aqueous feed to the organic under the conditions tested.

The loaded organic can be stripped with $1.7M H_2SO_4 + 1M Na_2SO_4$ with four five-minute contacts at A/O=1 if the Sn:Rh molar ratio in the loaded organic is sufficiently high (about 12:1). Here also, the Rh and the Sn follow one another as they are co-stripped at a Sn:Rh molar ratio of 2:1. The subsequent separation of Rh and Sn and the recovery of Rh have not yet been studied but will be examined in the course of the Ph.D. work which is to follow. The excess Sn in the organic which is not co-stripped with the Rh can be removed with a single hour-long 1M NaOH contact. The barren organic can then be recycled for further use after washing with HCl and H₂O.

APPENDIX A KINETICS

Let us consider the first aquation reaction:

and t = time in minutes

$$RhCl_{6}^{3} + H_{2}O = \frac{k_{1}}{k_{2}} RhCl_{5}(H_{2}O)^{2} + Cl^{-1}$$
 A.1

For the above reaction the following kinetic equation was determined (55):

$$-\frac{d[RhCl_{6}^{3}]}{dt} = k_{1}[RhCl_{6}^{3}] - k_{2}[RhCl_{5}(H_{2}O)^{2}][Cl^{3}] \qquad A.2$$
where $k_{1} = 0.11 \text{ min}^{-1}$
 $k_{2} = 0.013 \text{ min}^{-1} \text{ M}^{-1}$
at $T = 298 \text{ K}$

By solving the above equation (A.2), it would be possible to determine the concentration of both $RhCl_6^{3-}$ and $RhCl_5(H_2O)^{2-}$ at any given time assuming that the initial solution consisted solely of $RhCl_6^{3-}$ as the Rh complex.

The equation can be solved as follows if \in is taken as the fraction of $RhCl_5(H_2O)^{2}$ produced from $RhCl_6^{3}$ and if the chloride ion concentration is considered to be high enough that it is not significantly altered by the above exchange reactions. The above equation then becomes:

$$\frac{-d(1-\epsilon)}{dt} = k_1(1-\epsilon) - k_2[c1]\epsilon$$
A.3

$$\frac{d\epsilon}{dt} = k_1 - (k_1 + k_2[c1])\epsilon$$
A.4

$$\frac{(k_1 + k_2[c1])dt}{\epsilon e} = k_1 e$$
(k_1 + k_2[c1])dt

$$\frac{dt + c}{\epsilon e} = k_1 e$$

$$(k_1 + k_2[C1^-])t$$

 $\in e$
 $= \frac{k_1}{k_1 + k_2[C1^-]}e$
 $(k_1 + k_2[C1^-])c$
 $+ C A.6$

since at t=0,
$$\in=0$$
,
 $=(k_1 + k_2[Cl^{-}])t$
 $\in(t) = \frac{k_1}{k_1 + k_2[Cl^{-}]}$ (1 - e) A.7

$$[RhCl_{6}^{3-}] = (1-\epsilon) [RhCl_{6}^{3-}]_{mital}$$
 A.9
and $[RhCl_{5}(H_{2}O)^{2-}] = \epsilon [RhCl_{6}^{3-}]_{mital}$ A.10

Tables A.1 to A.3 list the concentration of each species as a function of time for a given total chloride ion concentration.

Table A.1: Calculation of Abundance of Rh Chloro-complexes at various times in 1M Cl [·] Solutions [Rh] _{tot} = 4×10^{-3} M (≈ 400 ppm) and [Cl [·]] = 1M ($\in_{max} = 0.894$)						
t $\in [RhCl_6^{3.}]$ [RhCl_6(H ₂ O) ^{2.}] (x10 ⁻³) (x10 ⁻³)						
0 0 4.00 0.00						
5 0.411 2.35 1.64						
10 0.633 1.47 2.53						
30 0.872 0.51 3.49						
60 0.893 0.43 3.57						
90 0.894 0.42 3.58						

The solution has virtually reached equilibrium at 60 minutes.

Table A.2: Calculation of Abundance of Rh Chloro-complexes at various times in 4M Cl Solutions $[Rh]_{tot} = 4x10^{-3}M (\approx 400 \text{ ppm}) \text{ and } [C1^{-}] = 4M$ ($\in_{max} = 0.679$) $[RhCl_{6}^{3}]$ (x10⁻³) e $[RhCl_{5}(H_{2}O)^{2}]$ t $(x10^{-3})$ 0 0 4.00 0.00 5 0.377 2.49 1.51 15 0.619 1.52 2.48 1.31 30 0.674 2.69 60 0.679 1.28 2.72

The solution has reached equilibrium at 60 minutes.

$\frac{\text{Table A}}{\text{various}}$ $[Rh]_{\text{tot}} =$ $(\in_{\max} = 0)$	<u>.3: Calculat</u> <u>times in 6M</u> 4x10 ³ M (≈ 4 0.585)	<u>ion of Abundance</u> <u>Cl'Solutions</u> OO ppm) and [Cl ⁻]	of Rh Chloro-complexes at = 6M
t	e	$[RhCl_{6}^{3}]$ (x10 ⁻³)	[RhCl ₅ (H ₂ O) ²⁻] (x10 ⁻³)
0	0	4.00	0.00
5	0.356	2.57	1.43
10	0.496	2.02	1.98
15	0.550	1.80	2.20
30	0.583	1.67	2.33
60	0.585	1.66	2.34

The solution has reached equilibrium at 60 minutes.

Similarly, the second aquation reaction can be considered:

RhCl₅(H₂O)^{2.} + H₂O
$$\stackrel{K_3}{=}$$
 RhCl₄(H₂O)^{2.} + Cl[.] A.11
K₄

The following rate equation was determined (56):

$$-\frac{d[RhCl_{5}(H_{2}O)^{2}]}{dt} = k_{3}[RhCl_{5}(H_{2}O)^{2}] - k_{4}[RhCl_{4}(H_{2}O)_{2}][Cl^{2}] A.12$$
where $k_{3} = 4.8 \times 10^{-3} \text{ min}^{-1}$
 $k_{4} = 3.84 \times 10^{-2} \text{ min}^{-1} \text{ M}^{-1}$
 $T = 298 \text{ K}$
and t = time in minutes

Similarly to the first reaction, Tables A.4 to A.6 below list the concentration of each species as a function of time for a given total chloride ion concentration.

$\frac{\text{Table A}}{\text{various}}$ $[Rh]_{tot} = (\epsilon_{max} = 0)$.4: Calcu] times in 4x10 ⁻³ M (≈).111)	<u>ation of Abundance of 1M Cl⁻ Solutions</u> 400 ppm) and [Cl ⁻] = 1	<u>Rh Chloro-complexes at</u> 1M				
t	e	$[RhCl_{5}(H_{2}O)^{2}]$ (x10 ⁻³)	[RhCl ₄ (H ₂ O) ²⁻] (x10 ⁻⁴)				
0 5	0.022	4.00 3.91	0.00 0.86				
10 15	0.039 0.053	3.84 3.79	2.10				
30	0.081	3.68	3.20				
120	0.110	3.55	4.40				
180	0.111	3.56	4.44				
The solution has about reached equilibrium at 120 minutes.							
Table A.5: Calculation of Abundance of Rh Chloro-complexes at various times in 4M Cl Solutions [Rh] _{tot} = 4×10^{-3} M (\approx 400 ppm) and [Cl] = 4M ($\in_{max} = 0.030$)							
t	E	$[RhCl_{5}(H_{2}O)^{2}]$ (x10 ⁻³)	$[RhCl_4(H_2O)_2] (x10^4)$				
0	0	4.00	0.00				
5	0.017	3.94	0.60				
10	0.024	3.90	0.96				
15	0.028	3.89	1.10				
60	0.030	3.88	1.20				
The solu	tion has n	reached equilibrium af	ter 30 to 60 minutes.				
Table A.6: Calculation of Abundance of Rh Chloro-complexes at various times in 6M Cl ⁻ Solutions [Rh] _{tot} = 4×10^{-3} M (≈ 400 ppm) and [Cl ⁻] = 6M ($\in_{max} = 0.020$)							
t	E	$[RhCl_{5}(H_{2}O)^{2}] (x10^{-3})$	[RhCl₄(H ₂ O) ₂ ⁻] (x10 ⁻⁴)				
0	0	4.00	0.00				
5	0.014	3.94	0.60				
10	0.019	3.93	0.74				
15	0.020	3.92	0.79				
30	0.020	3.92	0.82				

K,

The solution has reached equilibrium by 30 minutes.

APPENDIX B

<u>Conversion of Acidity Values to pH Values Using Jansz's Method</u> In order to group together the Rh extraction data that was obtained in the high acid region (0.7 to 8M HCl) with that obtained in the low acid region (pH 0.5 to 3.5), it was necessary to convert all of the acidity values to the pH scale. A very simple approach to accomplish this conversion could have been though the use of the following well known and used equation:

 $pH = -log[H^+] B.1$

In equation B.1, however, it is assumed that the concentration and the activity of H^+ are similar (that is, that the activity coefficient is very close to 1). In fact, for H^+ in chloride solutions, this is rarely the case unless the solutions are very dilute. Because pH measurements actually measure the activity of H^+ and not its actual physical concentration (such as molarity), it is important that the high acid values be converted to the pH scale with regard to their H^+ activity and not their physical H^+ concentration.

The acidity values of the raffinates were obtained through titrations with NaOH from which the H⁺ molarity levels could be back-calculated. In the following calculations, it was assumed that the molarity and molality of the raffinates were equivalent.

Jansz has proposed a methodology (70) to calculate the activity of H⁺ in relatively simple chloride based solutions from molality data. The details of this technique will not be covered here as this is not part of the subject matter of this research work, however, an overview of the conversion as it applies to the Rh-MgCl₂-HCl feeds will be presented.

Jansz has developed a series of calculations which can be solved to obtain the activity of H^+ in various chloride solutions including the case of a 1:2 and 1:1 cation:chloride electrolyte solution. Since the feeds were composed of MgCl, and HCl, Jansz's methodology could be used. In Jansz's publication (70), a graph of the activity of H^+ (y-scale) as a function of the total MgCl, concentration (x-scale) for a number of HCl solutions at different concentrations and temperatures is provided. It is therefore simple to convert the H⁺ concentrations to activities using this graph. Having measured the acidity through titration (which is equivalent to having measured the HCl concentrations) the HCl curve corresponding to the acidity measurement is located. Since the amount of MgCl, which was added to the feeds is known, the cross point of the MgCl, concentration and HCl curve is obtained and the H⁺ activity can then be directly read off the y-scale.

The calculated H⁺ activity can then be converted to the pH scale by using the more valid version of equation B.1: $pH = -log(\alpha_{H+})$ B.2

For the case where the HCl curves provided in Jansz's graph were too far for the measured HCl values (as for the 2.3M HCl feed), an approximate curve was drawn-in using an intermediate pure HCl activity provided by Jansz. Knowing where the new HCl curve originates at the y-axis and following the trend of all of the HCl curves provided by Jansz, it is reasonable to expect that the drawn-in curve is close to its true value and the final approximation of the activity of H+ obtained with this curve is probably quite close to that which would be obtained though the more complicated calculations also proposed by Jansz.

Table B.1 lists the values obtained throughout the calculations.

HCl (M) measured	MgCl ₂ (M) approximated	α _{H+} (from Jansz's graph)	pH (calculated using B.2)
0.53	1.7	1.9	-0.28
1.12	1.3	3.3	-0.52
2.33	0.6	6.8	-0.83

Table B.1: Measured and calculated values of HCl, MgCl₂ and H^+ to convert from concentration to activity and pH

APPENDIX C Rh Extraction with Cyanex 923

Similarly to the study performed with 8-hydroxyquinoline, the possibility of extracting Rh(III) from chloride solutions with a phosphine oxide extractant was studied. The extractant chosen was Cyanex 923, also referred to as TOPO (Chapter 4.1). Although it is well known that TOPO is a solvating extractant, it was judged feasible to try it for the extraction of Rh from acidic solutions since TOPO being a weak basic molecule (71) could become protonated under strong acidity (Figure C.1). TOPO is below amines in terms of basicity but above all other extractants such as TBP, ketones and ethers. As such, it was expected to be more selective than amines but still capable of extracting Rh(III).

Figure C.1: Schematic of Possible Protonation of TOPO

C.1 Effect of Acidity and Chloride Addition

Similarly to the R-HQ tests, the extraction of Rh with TOPO from solutions whose acidity ranged from 0.7 to 8M HCl was performed. It was found that for both fresh and 3 day aged solutions, Rh was not extracted by TOPO in this acidity range.

The non-extraction of Rh may be taken as an indication that the protonation of the organic is not strong enough to allow TOPO to extract Rh as an ion-pair even at high acidities. Moreover, it is possible that steric effects could also have played a role in this respect as well. The effect of the presence of a total chloride ion concentration of 4M on the extraction of Rh was studied in the 0.7 to 2.7 M HCl acidity range and similarly to the results obtained for the solutions without extra chloride, Rh was not extracted from either the fresh or the aged solutions. Evidently, TOPO cannot be used as a simple, direct extractant for Rh from acidic chloride solutions.

As with the R-HQ system, it became more and more evident that it would not be possible to find a simple extractant for Rh since many such reagents have already been experimented with and reported as ineffective in the literature. Once again, the focus of the search shifted from the organic phase to the aqueous phase by making use of Sn(II) to form the "reactive" Rh species. Similarly to the R-HQ system, the behaviour of a Rh-Sn(II)-Cl system was examined with, this time, Cyanex 923 as the extractant.

C.2 Effect of Acidity with 0.1M SnCl₂

The extraction of Rh from aqueous solutions ranging in acidity from 0.7 to 8M HCl and treated (as described in Chapter 4.2) with 0.1M $SnCl_2$ was determined and the results are shown in Figure C.2. Clearly, the extraction was dependent on the HCl concentration in the feeds with the extraction being nearly complete at 0.7M HCl and then gradually declining to virtual non-extraction as the acidity level was increased to 8M HCl.

Comparison of the results for a fresh solution versus a 3 day aged solution show that similarly to the R-HQ results, there was not a great difference in extraction degree between the fresh and aged solutions and that the same acidity trend was exhibited.

Figure C.2: Rh Extraction with SnCl₂ and Cyanex 923



^{0.1}M Sn, A/O=1, 10 min CT 300 ppm Rh feeds

The decrease in extraction degree with increasing HCl concentrations in the feed may be due to the increase in proton concentration, to the increase in total chloride concentration or to some other reason having to do with the specific behaviour of the Sn-activated Rh complex.

C.3 Effect of Chloride with 0.1M SnCl₂

In order to determine if the chloride concentration was responsible for the decrease in extractibility, the extraction of Rh from solutions of 0.7M HCl, with 0.1M $SnCl_2$ and with either 1 or 4 moles of extra chloride (from $MgCl_2$) was determined. The results are presented in Figure C.3. In fact, the extraction of Rh decreased significantly to only 43 and 29% for the 1 and 4M chloride solutions, respectively. The presence of large amounts of chloride ion definitely had a detrimental effect on the extraction of Rh from Rh-Sn-Cl solutions with TOPO.



C.4 Effect of SnCl₂ Concentration on Rh Extraction

Because the addition of 0.1M SnCl, is quite significant and in fact represents about a 25 times molar excess of Sn over Rh (when Rh is present at 400 ppm or 4×10^{-3} M), it was believed that the Sn concentration could be substantially lowered without impairing the Rh extraction degree. The molar Sn:Rh ratio was lowered to 3.2:1 and 6.3:1 and the Rh extraction degree was compared to that obtained when 0.1M Sn was added. The results are presented in Figure C.4. Although it is clear that there are not enough data points in this figure to safely determine the necessary Sn:Rh molar ratio for quantitative Rh extraction, this figure suggests that the ratio must be quite high since even at 6:1, only about 35% Rh extraction is achieved. This finding is quite contrary to that of the R-HQ system where a 2:1 Sn:Rh molar ratio is sufficient (Figure 5.28).



Figure C.4: Rh Extraction Dependance on the Sn:Rh Molar Ratio in the Feed

C.5 Stripping of Rh-Sn Complex Extracted by Cyanex 923

Having determined that Rh can be extracted with TOPO at 0.7 M HCl with low total chloride levels when $0.1M \text{ SnCl}_2$ was added to the feed, the stripping characteristics of this system were studied. Most of the strip solutions which were tested involved either high acidity or a high total chloride ion concentration. Table C.1 lists the Rh and Sn percent extracted and percent stripped for a series of different tests.

It is important to remember when studying the following table that for most of the tests, 0.1M SnCl₂ was added and therefore 30% Sn extraction versus 80% Rh extraction actually represents much more Sn than Rh in the organic .

Ĩ

	358n :Rh	358n: Rh	358n :Rh	2.88n :Rh	6.38n :Rh	1.3Cl	3.8C 1
Rh %X	82.3	80.0	75.7	21.2	33	43	29
Sn %X	33.3	31.5	31.9	33	25	22	23
1.7M HCl + MgCl ₂							
Rh %S	46	49					
Sn %S	15	23					
5.5M HC1							
Rh %S	8	16					
Sn %S	16	not deter- mined					
2M MgCl ₂							
Rh %S			9				
Sn %S			2				
H ₂ O							
Rh %S			crud				
Sn %S			crud				
1.7M HCl							
Rh %S				45	34	8	27
Sn %S				35	34	16	23

Table C.1:Summary of TOPO Exploratory Extraction and Stripping Tests (X = extraction, S = stripping)

The main points to remark from the results presented in Table C.1 are that in order to achieve quantitative Rh extraction, a significant excess of Sn was required and a low concentration of chloride ions was necessary. From the industrial point of view, this is not the desired situation since it can be expected that the Rh feed will contain a significant amount of chloride. Moreover, stripping from this system was with difficulties. For these reasons, the TOPO system was dropped in favour of the R-HQ system already discussed in Chapter 5.3.

REFERENCES

- 1. J.R. Loebenstein, <u>Mineral Facts and Problems</u>, US Bureau of Mines, Bulletin 675, 1985, p.595.
- 2. M.J. Cleare, P. Charlesworth, and D.J. Bryson, J. Chem. Biotechnol., 1979, **29**, p.210.
- 3. R.A. Grant, The Separation Chemistry of Rhodium and Iridium, in L. Manziek (editor), Precious Metal Recovery and Refining, International Precious Metals Institute (IPMI), 1990, p.7.
- G.B. Harris, The Refining of Gold and Precious Metals, Refining and Recycling of Precious Metals - A Technology Update, Professional Development Seminar, McGill University, April 1991, p.23-40.
- 5. G.P. Demopoulos, CIM Bulletin, 1989, 82 (923), p.165.
- 6. D.S. Flett, Solvent Extraction in Hydrometallurgy, in <u>Hydrometallurgy: Research, Development and Plant</u> <u>Practices</u>, (Editors, K. Osseo-Asare and J.D. Miller), TMS-AIME, Warrendale, 1983, p.39.
- 7. E.W. Stern, Symp. on Recovery, Reclamation and Refinig of Precious Metals, G.Foo and M.E. Browning, eds., IPMI, Allentown, Penn., paper No. 1, March 1981.
- D.C. Job, "An Outlook on Precious Metal Markets", Refining and Recycling of Precious Metals - a Technology Update, Professional Development Seminar, McGill University, April 1991.
- S.I. Ginzberg et al., <u>Analytical Chemistry of the</u> <u>Platinum Metals</u>, Wiley, New York, 1975, pp 102-106, 434-458.
- D.A. Palmer and G.M. Harris, Inorganic Chemistry, 1975, 14 (6), p.1316.
- 11. R.I. Edwards and W.A.M. te Riele, "Commercial Processes for Precious Metals" in <u>Handbook of Solvent Extraction</u>, T. Lo, M.H.I. Baird and C. Hanson (Eds.), Wiley-Interscience, New York, 1983, pp 725-732.
- 12. H. Moriyama, T. Aoki, S. Shinoda and Y. Saito, J. Chem. Soc., Dalton Trans., 1981, p.639.
- 13. S.J. Al-Bazi and A. Chow, Talanta, 1984, 31 (10A), p.815.

ſ

- 14. G.B. Harris and R.W. Stanley, "Hydrometallurgical Treatment of Refinery Anode Slimes", in Precious Metals 1986, Ed. U.V. Rao, Proceedings of the 10th IPMI Conference, Lake Tahoe, Nevada, June 1986, p.239.
- 15. W.P. Griffith, <u>The Chemistry of the Rarer Pt Metals</u>, Interscience Publishers, New York, 1967, p.323.
- 16. K.F.G. Brackenbury, L. Jones, I. Nel, K.R. Koch and J.M. Wyrley-Birch, Polyhedron, 1987, 6(1), p.71.
- 17. M. Mojski, Talanta, 1980, 27, p.7.
- 18. H. Forster and I. Schoefer, J. of Radioanalytical Chem., 1975, 28, p.153.
- 19. A. Diamantatos and A.A. Verbeek, Anal. Chim. Acta, 1977, 91, p.287.
- 20. R.M. Uttawar and A.P. Joshi, J. of Indian Chem. Soc., 1981, 58, p.898.
- 21. A. Diamantatos, Anal Chim. Acta, 1983, 147, p.219.
- 22. M.A. Khattak and R.J. Magee, Anal. Chim. Acta., 1969, 45, p.297.
- 23. L. Jones, I. Nel and K.R. Koch, Anal. Chim. Acta., 1986, 182, p.61.
- 24. D.M. Adams and P.J. Chandler, Chem Ind. (London), 1965, p.269.
- 25. S. Iwasaki, T. Nagai, E. Miki, K. Mizumachi and T. Ishimori, Bull. Chem. Soc. Jpn., 1984, 57, p.386.
- 26. S.C. Dhara, Solvent Extraction of Precious Metals with Organic Amines, in <u>Precious Metals: Mining,</u> <u>Extraction, and Processing</u>, (Editors, V. Kudryk, D.A. Corrigan and W.W. Liang), TMS-AIME, Warrendale, February 1984, p.199.
- 27. N.V. Fedorenko and T.I. Ivanova, Russian Journal of Inorganic Chemistry, 1965, **10** (3), p.387.
- 28. V.I. Dolgikh, P.I. Borikov, V.F. Borbat, E.F. Kouba and L.M. Gindin, Tsvet. Metal, 1967, 40, p.30.

29. Hu Longxing, Study of Solvent Extraction Kinetics of Rh(III) with Trialkyl Methylammonium Chloride N₂₆₃, Graduate Division, Shanghai University of Technology, Shanghai, China.

Υ.

ſ

- 30. R.A. Grant and B.A. Murrer, 1988, Extraction of Metals, United States Patent 4,726,841.
- 31. M.A. Khan and D.F.C. Morris, J. Less Common Metals, 1967, 13, p.53.
- 32. P.A. Lewis, D.F.C. Morris, E.L. Short and D.N. Waters, J. Less Common Metals, 1976, **45**, p.193.
- 33 E.W. Berg and W.I. Senn, Anal. Chim. Acta., 1958, 19, p.109.
- 34. E.W. Berg and E.Y. Law, Anal. Chim. Acta., 1962, 27, p.248.
- 35. Y. Baba, K. Inoue, K. Yoshizuka and I. Nagamatsu, Proceedings of Symposium of Solvent Extraction 1988, Tokyo Institute of Technology, Tokyo, 1988, p.37.
- 36. A.I. Busev and V.K. Akimov, Talanta, 1964, 11, p.1657.
- 37. I. Longden, N.M. Patel, and J. Thornback, Solvent Extraction and Ion Exchange, 1986, 4, p.421.
- 38. N.M. Patel and J.R. Thornback, Solvent Extraction and Ion Exchange, 1987, 5, p.633.
- 39. Y.A. Zolotov, O.M. Petrukhin, V.N. Shevchenko, V.V. Dunina and E.G. Rukhadze, Anal. Chim. Acta., 1978, 100, p.613.
- 40. B.R. Acharyya, S. Das and S.P. Bag, Indian J. of Chem., 1990, **29A**, p.298.
- 41. A. Diamantatos, Anal. Chim. Acta, 1981., 131, p.53.
- 42. A. Diamantatos, Anal. Chim. Acta, 1973, 67, p.317.
- 43. F.E. Beamish, A critical review of methods of isolating and separating the noble metals - II: Ion exchange and solvent extraction, 1967, Talanta, 14, p.991.
- 44. K. Brajter, K. Kleyny and Z. Vorbrodt, 1980, Talanta, 27, p.433.

- 45. J.H. Ruckman, Precious Metals 1989, Ed. B. Harris, Proceedings of the 13th IPMI Conference, Montreal, Quebec, June 1989, p.381.
- 46. R.L. Bruening, S.R. Izatt and I.D. Griffin, Precious Metals 1990, Ed. D.A. Corrigan, Proceedings of the 14th IPMI Conference, San Diego, California, June 1990, p.97.
- 47. F.R. Hartley, C. Burgess and R.M. Alcock, <u>Solution</u> <u>Equilibria</u>, Ellis Horwood Ltd., Chister England, 1st Ed., 1980, p.20-25.
- 48. D. Cozzi and F. Pantani, Journal of Inorganic and Nuclear Chemistry, 1958, 8, p.385.
- 49. M.H. Mihailov, V.Ts. Mihailova and V.A. Khalkin, Journal of Inorganic and Nuclear Chemistry, 1974, 36, p.115.
- 50. M.H. Mihailov, Journal of Inorganic and Nuclear Chemistry, 1974, 36, p.107.
- 51. D.D. DeFord and D.N. Hume, J. Am. Chem. Soc., 1951, 73, p.5321.
- 52. L. Riccoboni, P. Papoff and G. Arich, Gazz. Chim. Ital., 1949, 79, p.547.
- 53. E. Hogfeldt, <u>IUPAC Stability Constants of Metal-Ion</u> <u>Complexes, Part A, Inorganic Ligands</u>, Pergamon Press, 1982, p.214.
- 54. L. Sillen, <u>Stability Constants Supplement No.1, Part 1,</u> <u>Inorganic Ligands</u>, The Chem. Soc. of London, 1971, p.174.
- 55. W. Robb and G.M. Harris, Journal of the American Chemical Society, 1965, 87, p.4472.
- 56. W. Robb and M.M. de V. Steyn, Inorganic Chemistry, 1967,
 6, p.616.
- 57. <u>Stability Constants</u>, The Chem. Soc. of London, 1964, p.283.
- 58. G.P. Dempoulos and P.A. Distin, Hydrometalllurgy, 1983, 11, p.389.
- 59. B. Côté, Ph.D. work, McGill University, in progess.
- 60. Cyanamid Co, Niagara Falls, Ontario, Cyanex 923 Extractant Data Sheets #87-2-830 3k 8/87.

- 61. G.P. Dempoulos, N. Kuyacak, D.L. Gefvert and M.H. Richter, Precious Metals 1989, Ed. B. Harris, Proceedings of the 13th IPMI Conference, Montreal, Quebec, June 1989, p.210.
- 62. G. Pouskouleli and G.P. Demopoulos, "Recovery and Separation of Pt and Pd by Coextraction and Differential Stripping" in <u>Separation Processes in Hydrometallurgy</u>, Ellis Horwood Ltd, Manchester, U.K., 1987, p.174.
- 63. G.P. Dempoulos, Journal of Metals, June 1986, p.13.
- 64. V.H. Aprahamian, G.P. Demopoulos and G.B. Harris, Precious Metals 1991, Proceedings of the 15th IPMI Conference, Naples, Florida, June 1991, to be published.
- 65. D.J. Shaw, <u>Introduction to Colloid and Surface Chemistry</u>, 3rd Ed., Butterworths, London, 1980, p.70.
- 66. C.J. KIng, <u>Separation Processes</u>, 2nd Ed., McGraw-Hill, New York, 1980, p.633.
- 67. Z. Wu, S. Yu and J. Chen, ISEC 1986, <u>International</u> <u>Solvent Extraction Conference Preprints</u>, II, p.II-447.
- 68. V.H. Aprahamian, M.Eng. thesis, McGill University, in preparation.
- 69. A.G. Davies, G. Wilkinson and J.F. Young, J. Am., Chem., Soc., 1963, 85, p.1692.
- 70. J.J.C. Jansz, Hydrometallurgy, 1983, 11, p.13.
- 71. G.M. Ritcey and A.W. Ashbrook, <u>Solvent Extraction:</u> <u>Principles and Applications to Process Metallurgy</u>, Part 1, Elsevier Scientific Pub., New York, 1978, p.148.