

# Recovery of platinum, palladium and gold from a pregnant cyanide heap leach solution, with the use of ion exchange resins

*by*

Ebon Schoeman

Thesis presented in partial fulfillment  
of the requirements for the Degree

*of*

MASTER OF SCIENCE IN ENGINEERING  
(EXTRACTIVE METALLURGICAL ENGINEERING)



in the Faculty of Engineering  
at Stellenbosch University

*Supervisor*

Prof Steven Bradshaw

*Co-Supervisor*

Prof Guven Akdogan

December 2012

# Declaration

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# Abstract

The aim of this study was to evaluate the feasibility of recovering platinum, palladium and gold from a heap leach cyanide solution, with the use of commercially available ion exchange resins.

The pregnant leach solution contained low concentrations ( $< 0.4$  ppm) of platinum, palladium and gold, with higher concentrations ( $> 5$  ppm) of base metals such as iron, copper, nickel and zinc. Twelve commercially available ion exchange resins were screened for the investigation. It was found that strong base anion exchange resins exhibited the highest recovery potentials for platinum, palladium and gold from the cyanide solution. From the screening results four strong base anion exchange resins were selected for further investigation, namely, Dowex 21K XLT, Amberjet 4600, Amberlite PWA-5 and Minix. The selection was made on the basis of high platinum, palladium and gold recovery potentials, and also in order that different exchange capacities and functionalities could be compared during the study.

Initial adsorption test work involved batch kinetic studies, isotherm evaluations and repeated loading experiments in respect of the four resins. It was found that the exchange capacity and functionality of the strong base anionic resins played a significant role in their affinity for different anions in solution. Strong base resins that contained higher exchange capacities and smaller functionalities were found to recover all metal anions in solution in a non-selective manner. However, strong base anion exchange resins that contained lower exchange capacities and larger functionalities were found to have a higher affinity for lower charged anions such as  $Au(CN)_2^{-2}$ ,  $Pt(CN)_4^{2-}$  and  $Pt(CN)_4^{2-}$  over other metal cyanide anions present in the solution. Thus on this basis, only Amberlite PWA-5 and Minix were selected to be investigated further, with the elimination of Dowex 21K XLT and Amberjet 4600 from the study.

The temperature and pH of the solution did not affect the loading of platinum, palladium and gold on both Minix and Amberlite PWA-5. However, an increase in solution temperature improved the loading kinetics of platinum, palladium and gold from the cyanide solution. Zinc and nickel concentrations in the cyanide solution affected the loading of platinum, palladium and gold, which is a result of the cyanide complexes of zinc and nickel,  $Ni(CN)_4^{2-}$  and  $Zn(CN)_4^{2-}$ , being similar to the cyanide complexes of platinum,

palladium and gold. An increase in the feed concentrations of platinum, palladium and gold significantly improved both the loading kinetics and loading of these metals onto both Amberlite PWA-5 and Minix.

Three eluants namely zinc cyanide, potassium thiocyanate and acidic thiourea, were investigated for the elution of platinum cyanide, palladium cyanide and aurocyanide from Minix and Amberlite PWA-5. Effective elution of platinum cyanide and palladium cyanide could be achieved with the use of zinc cyanide and thiocyanate; however, slow elution of aurocyanide was noted with the use of these two eluants. Acidic thiourea could effectively elute palladium and gold from the resins; however, poor elution of platinum was noted with the use of acidic thiourea. It was concluded that this was the result of a kinetic effect on the reaction between  $Pt(CN)_4^{2-}$  and thiourea, due to the low pH of the acidic thiourea solution. During the investigation on the effect of eluant concentration, elution temperature and elution flow rates on the elution of platinum, palladium and gold from strong base resins, it was found that the concentration of the eluants was the only parameter that had a noticeable effect on the elution of these metals.

Overall it was concluded that effective recovery of platinum, palladium and gold from a cyanide solution containing low concentrations ( $< 1\text{ppm}$ ) of these metals is possible with the use of commercially available strong base anion exchange resins. A possible pre-concentration step, prior to adsorption, should however be investigated to improve the loading kinetics and loading of these metals on the resins. An acid wash step is also recommended, to eliminate excessive amounts of zinc and nickel in the eluate during the process. It is also recommended that a preliminary cost-analysis of the process be performed, to compare ion exchange with other processes such as adsorption onto activated carbon and zinc cementation.

# Opsomming

Die doel van hierdie studie was om die adsorpsie van platinum, palladium en goud uit 'n loogsianiedoplossing te evalueer, met die gebruik van ion-uitruilings harse.

Die swanger loogoplossing het platinum, palladium en goud in lae konsentrasies (< 0.4ppm), met hoë konsentrasies (> 10ppm) van basis metale, sink, koper, yster en nikkel, bevat. Twaalf kommersieël beskikbare harse is gekeur vir die ondersoek. Daar is bevind dat sterk basis anioon-uitruilings harse die hoogste edelmetaal adsorpsie potensiaal vanuit die sianiedoplossing gehad het. Vanuit die keuringsresultate is vier sterk basis anion-uitruilings harse, naamlik, Dowex 21K XLT, Amberjet 4600, Minix en Amberlite PWA-5 gekies vir verdere ondersoek. Die harse was gekies op die basis van hoë edelmetaal adsorpsie potensiaal, en ook om harse met verskillende kapasiteite en funksionaliteite te hê.

Aanvanklike adsorpsie eksperimente het kinetiese studies, isoterm evaluasies en herhaalde lading eksperimente behels. Daar is bevind dat funksionaliteit en kapasiteit, 'n belangrike rol speel in die affiniteit wat die harse vir verskillende metaalanione in die oplossing het. Sterk basis anioon-uitruilings harse met hoër kapasiteite en kleiner funksionaliteite het nie-selektiewe adsorpsie getoon. Die harse met laer kapasiteite en groter funksionaliteite was egter selektief vir die metaalanione in 'n laer valente toestand, soos die van platinum, palladium, goud, koper en nikkel. Vanuit die resultate is daar besluit om slegs aan te gaan met eksperimentering, met die gebruik van Amberlite PWA-5 en Minix.

Temperatuur en pH het geen invloed gehad op die lading van platinum, palladium en goud nie. Daar was egter 'n positiewe effek op die kinetika van die drie edelmetale, met 'n verhoging in temperatuur. Verhoging in die sink en nikkel konsentrasies het beide die lading en kinetika van platinum, palladium en goud negatief beïnvloed. Die rede hiervoor kan toegeken word aan die anione van sink en nikkel,  $Ni(CN)_4^{2-}$  en  $Zn(CN)_4^{2-}$ , wat soortgelyk is aan die komplekse van platinum, palladium en goud. Verhogings in die konsentrasies van platinum, palladium en goud in voeroplossing het 'n positiewe effek op beide die lading en kinetika van al drie edelmetale gehad.

Drie elueringsoplossings, naamlik, sinkcyanied, kaliumsianaat en suur thiourea, is ondersoek vir die eluering van platinumsianied, palladiumsianied en goudsianied van Amber-

lite PWA-5 en Minix. Effektiewe eluering van platiniumsianied en palladiumsianied was moontlik met die gebruik van sinksianied en sianaat, maar die eluering van goudsianied was stadiger as die van platiniumsianied en palladiumsianied. Suur thiourea kon palladium en goud effektief van die harse verwyder, maar geen platinum eluering was moontlik met die gebruik van suur thiourea nie. Die rede hiervoor is dat daar 'n kinetiese effek geplaas is op die reaktiwiteit van platiniumsianied in die suuroplossing. Daar is gevind dat die elueringsoplossing konsentrasie die enigste noemenswaardige effek op die eluering van die drie edelmetale gehad het.

Algeheel het die studie bewys dat effektiewe ekstraksie van platinum, palladium en goud uit 'n sianiedoplossing moontlik is met die gebruik van kommersieël beskikbare anioonuitruilings harse. 'n Moontlike konsentrasie stap voor adsorpsie kan ondersoek word om die lading en kinetika van die edelmetale te bevorder. 'n Suurwas voor eluering word ook voorgestel om die onedelmetale te verwyder van die hars voor die eluering van platinum, palladium en goud. Laastens moet 'n koste-analise gedoen word om die proses met ander prosesse soos geaktiveerde koolstof en sink sementasie te vergelyk.

# Acknowledgements

A special thanks goes to Professor Steven Bradshaw and Professor Guven Akdogan for their guidance and support throughout my postgraduate project. Thanks also goes to Neil Snyders and Professor Jacques Eksteen as well as my fellow colleagues in the Akanani research group, for their support and ideas. I would also like to thank the workshop staff, especially Alvin Peterson, for providing me with the necessary work space and equipment needed for my experiments. I would like to thank miss Hanlie Botha and miss Riana Rossouw for their help with my sample analysis.

I want to thank Lonmin Plc. (Western Platinum) for their financial support that made this project possible.

I want to acknowledge every member of my family, especially my father and mother, for their support and motivation during my studies. I would also like to thank my beautiful wife, Mariska, for her support, understanding and patience during the course of this project, I appreciate it more than you know.

Lastly, I want to thank my heavenly Father, for giving me the ability, strength, health and surrounding me with supporting people that enabled me to complete this project of which I am most proud of.

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# Chapter 1

## Introduction

### 1.1 Project Background

The project originated from the recovery of platinum group metals (PGMs) from low-grade PGM-bearing material in the Bushveld Igneous Complex. With depletion of the shallower, high-grade South African PGM reserves, new resources at greater depths or in areas with geological complexity, have to be explored. These new resources however, consist of more complex mineralogies and thicker reefs, compared with the narrow reef Merensky and UG2 deposits. A major resource of PGMs that remains poorly exploited is the Platreef orebody northwest of Mokopane in South Africa. Anglo American Platinum is currently the only mining company with active mining activity in the area, with other companies having prospecting rights along strike of the area.

The Platreef ore body is a large orebody of between 20 and 100 meters in thickness, with variable composition, mineralogy and hardness. The reef has a reasonable head grade (3E+Au) of between two to six grams per ton. However, traditional mill-float-mill-float (MF2) approaches to milling and flotation-produced concentrates of low grade, and high mass pulls are required to achieve sufficient recovery of the valuable metals. The reef is also predominately a base metal and palladium resource by composition, rather than the traditional platinum resource, which will lead to marginal economics. In addition to the above mentioned factors, the remoteness of the site, limited infrastructure and lack of skilled labour present obstacles. Thus, unless a high grade concentrate, comparable to the Merensky concentrate grades, can be produced economically, or significant increase in the price of palladium occurs, the capital and operating costs of a mill-float-smelt-refine option would be significant. These factors motivate a study into the direct leaching of concentrate or ore, as an alternative to smelting.

One of the approaches considered for processing low-grade material is heap leaching. If successful, heap leaching can be applied, even if high-grade and low-grade material are



produced, from which the low-grade material can be heap leached. However, because of the amount of base metals present in the reef compared with the PGMs, an alternative process option has to be considered for removing these metals from the material, prior to the PGM recovery. It has been proposed that a sequential heap leach be performed, which will entail a heap bioleach and a high temperature cyanide leach (Mwase *et al.*, 2012). The main goal of the bioleach will be to remove most of the base metals from the material, from where the PGMs can be extracted from the residue of the bioleach, using a subsequent cyanide leach.

Recent research on low-grade concentrate by Mwase *et al.* (2012) showed the effectiveness of a two-stage heap leach for the extraction of PGMs and base metals from low grade, high chromium, UG2 concentrate. Base metals, such as copper, iron, nickel and cobalt, could be extracted to a sufficient degree from the material, prior to the cyanide leach. The extraction of PGMs from the material with cyanide was slow, especially the dissolution of platinum, compared to that of palladium and gold. It was also observed that noticeable amounts of base metals still present in the residue material from the bioleach, were co-extracted with the PGMs during the cyanide leach.

The investigation performed in the current study directly stemmed from the upstream leaching processes for the recovery of base metals from the pregnant bioleach solution and the recovery of platinum, palladium and gold from the pregnant cyanide leach solution. The base metal recovery options include ion exchange, selective precipitation, solvent extraction and molecular recognition technology, whereas the PGM recovery processes, include ion exchange, adsorption onto activated carbon and zinc cementation. During this study ion exchange was investigated for the recovery of aurocyanide, platinum cyanide and palladium cyanide from the pregnant leach solution.

## 1.2 Project Overview

Ion exchange resins have sparked significant interest in their use for the recovery of valuable metals, such as gold and silver, from cyanide solutions over the past few decades, as an alternative to the carbon-in-pulp (CIP) process. Activated carbon is the most widely used adsorbent for the recovery of these metals from cyanide solutions. However, due to difficulties with the process, resin-in-pulp (RIP) and resin-in-solution (RIS) technology is now being considered as the next generation process for the recovery of valuable metals from cyanide solutions (Fleming, 1993, 1998; Van Deventer *et al.*, 1999). A number of comparable studies on the two adsorption processes have been performed and the conclusion drawn from these studies was that ion exchange resins were superior to activated carbon with respect to loading capacity, loading kinetics and also capital and operating

costs.

Most of the research on the recovery of metals from cyanide solutions, focused on gold recovery from cyanide solutions (Fleming and Cromberge, 1984*c,b*; Kotze *et al.*, 2005). Little information is available on the recovery of platinum and palladium from cyanide solutions using ion exchange resins. The reason for this is the slow dissolution of platinum during cyanidation (Sibrell and Atkinson, 1994), which results in the extraction of PGMs from PGM-bearing material with the use of cyanide and their subsequent recovery from the pregnant leach solution (PLS) to be uncommon in practice. Thus, unlike the gold and silver industry, where ion exchange resins have found widespread application for the recovery of these metals from cyanide solutions, similar approaches have not been established for the PGM industry.

To that effect, the aim of this study was to demonstrate the effectiveness or ineffectiveness of using commercially available ion exchange resins for the recovery of platinum, palladium and gold from a cyanide solution dilute in them ( $< 0.4$  ppm), and producing a process stream that can be sent directly to a refinery.

The study experimentally evaluated different commercially available resins, for the recovery of platinum, palladium and gold from the pregnant cyanide leach solution. Different eluting agents for the removal of these cyanide complexes were also evaluated.

### 1.3 Research Questions

The key questions for this investigation were:

- Can commercially available ion exchange resins be used for the recovery of platinum and palladium from cyanide solutions dilute in them?
- How would the base metal cyanides also present in the solution affect the recovery of platinum, palladium and gold?
- What platinum, palladium and gold loadings on ion exchange resins can be expected?
- Can the platinum cyanide and palladium cyanide be removed from the loaded ion exchange resins, and if so, what is the most effective elution method?

### 1.4 Objectives

During literature study, it was recognized that previous studies performed on the recovery of platinum and palladium from cyanide solutions consisted only of qualitative discussions

on the subject, and that no in-depth investigation was performed on the process. In addition, previous work was done on cyanide solutions that were more concentrated in platinum and palladium (150 ppm to 500 ppm), and thus it is unknown if ion exchange resins will be effective in recovering these metals from low grade ( $< 0.4$  ppm) cyanide solutions. No published work on the subsequent elution of platinum and palladium cyanides from ion exchange resins could be found. Taking all of the above mentioned aspects into account, this study aimed to:

- Evaluate different types of commercially available ion exchange resins, and compare their platinum and palladium recovery potentials, in order to select the most effective resins for the investigation,
- Investigate the possibility to selectively recover the precious metals over the other metals present in the pregnant leach solution (PLS),
- Evaluate the effect of different parameters on the adsorption of platinum cyanide, palladium cyanide and aurocyanide onto ion exchange resins,
- Investigate and compare different elution methods for the removal of platinum cyanide and palladium cyanide from the loaded resins,
- Assess the feasibility of ion exchange technology for the recovery of PGMs from cyanide solutions, by comparing it to other recovery processes such as adsorption onto activated carbon and zinc cementation,
- Produce a conceptual process flow diagram including different implications for the recovery of PGMs from a cyanide heap solution, with the use of ion exchange resins.

## 1.5 Thesis Structure

Chapter 2 presents an overview of the process that was investigated, along with a discussion on common processes for the recovery of platinum, palladium and gold from cyanide solutions. A detailed discussion on the aspects associated with ion exchange is given in Chapter 3. The experimental equipment and methodology are discussed in Chapter 4, followed by a discussion of the experimental results in Chapter 5 and 6. In Chapter 7, conceptual flow diagrams generated from the findings of the work performed, are discussed. The thesis is concluded with a summary of the main conclusions and recommendations in Chapter 8.

The appendices contain a list of publications arising from the work (Appendix A) and product data sheets for the four strong base anionic resins selected from the research (Appendix B).

## Chapter 2

# Cyanide Leaching and Common Recovery Processes

### 2.1 Cyanide Leaching

Cyanidation is the most common method used today for the recovery of gold from ore, with a substantial amount of research and studies available on the recovery of gold from ore via cyanide leaching. The process is well understood and established on commercial scale, both for low grade and high grade gold bearing material (Lakshmanan and Tackaberry, 1990; Hiskey, 1983; Muhtadi, 1988).

However, the recovery of platinum group metals from low grade concentrate using cyanide is a relative new concept, and has only find significant application in the recovery of these metals from recycled automobile catalyst (Desmond *et al.*, 1991; Kuczynski *et al.*, 1992; Roijals *et al.*, 1996; Shams *et al.*, 2004; Sibrell and Atkinson, 1995). However, the cyanide leaching performed in these studies was done at elevated temperatures and pressures, and not at the conditions typical of heap leaching. The main reason for such little application of cyanide as leaching agent for the recovery of platinum and palladium from PGM-bearing material is the slower and more difficult dissolution of platinum in cyanide solution compared to gold.

It is known that the linear aurocyanide complex ( $Au(CN)_2^-$ ) forms during extraction of gold by cyanide leaching. Literature on the cyanide leaching chemistry of platinum group metals proposes that the formation of square-planar cyanide complexes of platinum ( $Pt(CN)_4^{2-}$ ) and palladium ( $Pd(CN)_4^{2-}$ ) occur in pregnant cyanide leach solutions. The three cyanide complexes described above are the main focus of this project, not in terms of their recovery from the cyanide solution, but also their elution from ion exchange resins.

A simplified process flow diagram for the proposed process that was investigated is shown in Figure 2.1.

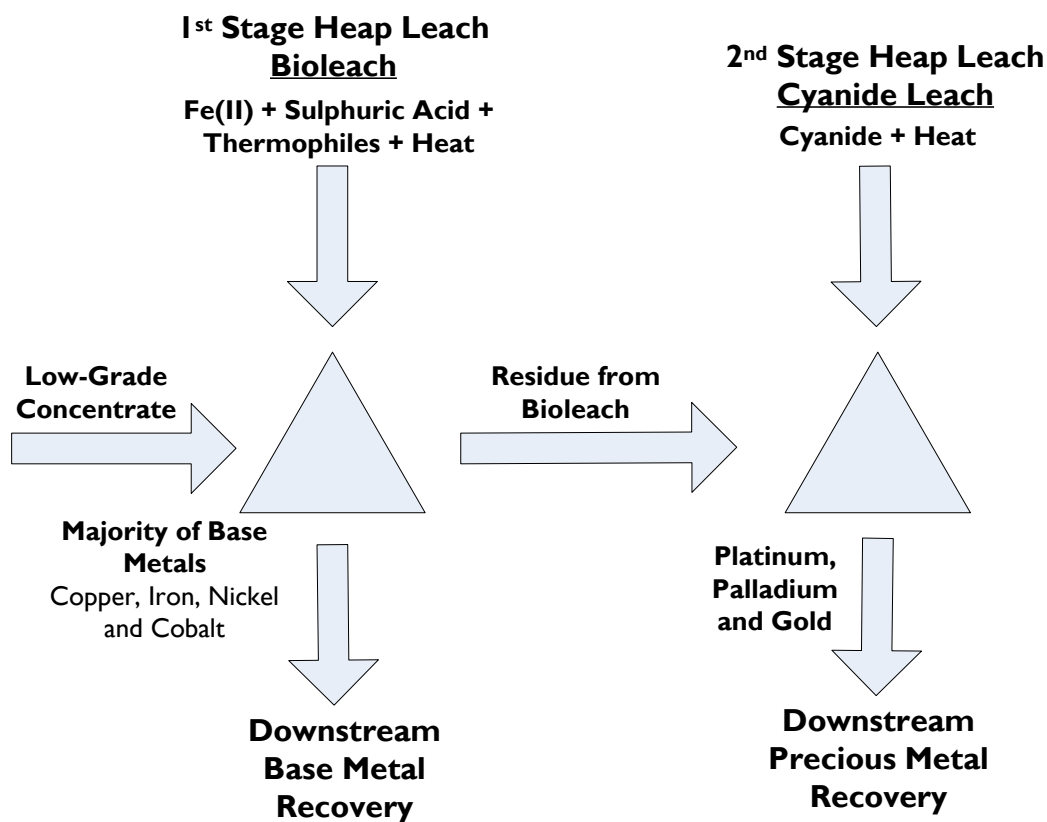


Figure 2.1: Simplified diagram for process investigated

From Figure 7.1, it can be seen that the first stage of the heap leach entails heap leaching low-grade concentrate with a solution consisting of sulfuric acid, thermophiles and ferric iron at  $65^{\circ}\text{C}$ . The main purpose of this heap leach is the removal of most of the base metals from the heap material. The residue from the bioleach is then transferred to a second heap where it is leached with a dilute cyanide solution at  $60^{\circ}\text{C}$ , to extract the gold, platinum and palladium. Table 2.1 and Table 2.2 show the material assays of concentrate that was used for leaching experiments conducted in a separate study, for platinum group metals, and base metals and gangue respectively (Mwase *et al.*, 2012).

Table 2.1: Platinum group metals (PGMs)

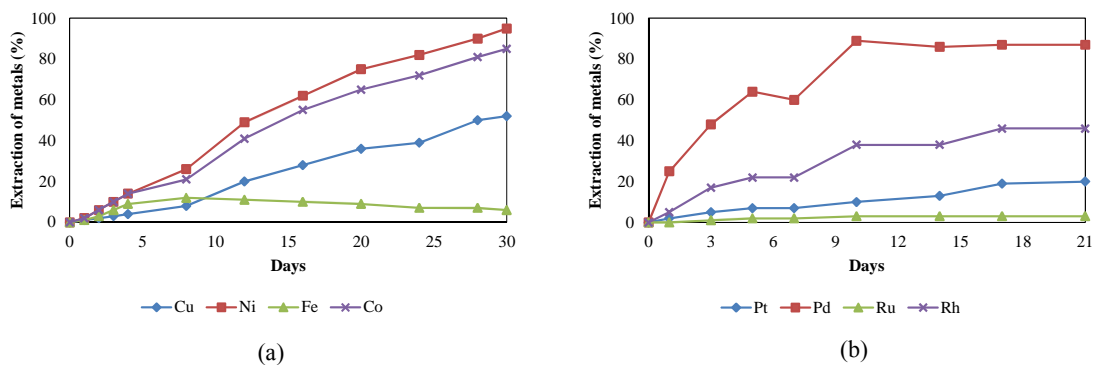
Concentration (g/t)			
Pt	Pd	Ru	Rh
12.	8.2	4.4	2.6

The low-grade concentrate was introduced to the bio-leaching agent in a column, with recycling of the leach solution through the material for seven days, after which it was replaced with fresh solution (Mwase *et al.*, 2012). The extraction profiles for the major

**Table 2.2:** Base and gangue metals

Fraction (%)								
Cu	Ni	Fe	Co	Mg	Al	Si	Ca	Cr
0.36	0.74	6.7	0.011	15.	1.1	25.	1.5	0.44

base metals and platinum group metals after 30 days of contact are represented in Figure 2.2 (a) and (b), respectively.



**Figure 2.2:** Extraction profiles obtained by Mwase *et al.*(2012) for (a) base metals and (b) PGMs

In Figure 2.2 (a), it is shown that extractions of 52% copper, 95% nickel and 85% cobalt were achieved in 30 days. Mwase *et al.*(2012) concluded that the bioleach process showed potential for processing concentrate at commercial level, and that the success of the process can be attributed to the fact that the base metals are largely present in the concentrate as sulphide minerals. The low iron in solution was concluded to be caused by iron precipitation under the conditions of the experiment (Mwase *et al.*, 2012).

In Figure 2.2 (b), it can be seen that co-extraction of PGMs occurred during the bioleach. However, extraction of the more valuable metal, platinum, was not significant after 30 days of bioleaching. The extractions of rhodium and ruthenium were, however, significant, which suggests investigating the recovery of these metals before or after the base metal recovery from the pregnant bioleach solution (Mwase *et al.*, 2012).

During subsequent leaching experiments performed by Mwase *et al.*(2012), the residue from the bioleach was leached with a cyanide solution, and the results for the cyanide leach after 21 days of leaching are presented in Table 2.3.

From Table 2.3 it is shown that sufficient extraction of palladium was achieved during 21 days of cyanide leaching. Platinum extraction was slow, compared with the other PGMs. However, the leach curve of platinum was linear, which suggested that the target extraction of platinum could be reached given a longer leaching time (Mwase *et al.*, 2012). The extraction of base metals that were still present in the material was high, with

**Table 2.3:** Extraction results for cyanide leach (Mwase *et al.*, 2012)

PGMs	Pt	Pd	Ru	Rh	
Extraction (%)	20.3	87	3.4	46	
Base Metals	Cu	Ni	Fe		
Extraction (%)	34	41	0.84		
Gangue	Mg	Ca	Cr	Al	Si
Extraction (%)	0.0038	0.38	0.0019	0	0.86

insignificant extraction of gangue elements. In this project the pregnant cyanide leach solution generated during the second-stage cyanide leach will be treated with ion exchange resins for the recovery of platinum, palladium and gold.

## 2.2 Common Precious Metal Recovery Processes

### 2.2.1 Zinc Cementation (Merrill-Crowe)

The oldest process for the recovery of gold and silver from cyanide solutions is zinc cementation, also known as the Merrill-Crowe process. The process is an established and well-known technology, that consists of four unit operations, namely, solution clarification, de-aeration, precipitation and precipitate filtration (Atwood and Atwood, 1985; Hiskey, 1983). The process operates on the principle that gold and silver are more noble than zinc, and thus they have the ability to reduce to their state of zero valence, rather than remaining in their respective cyanide complexes (Muhtadi, 1988).

In 1949, however, the process started to be threatened by activated carbon, with the commercialization of the first carbon-in-pulp (CIP) plant, for the recovery of gold, at the San Andreas de Copan plant in Honduras (Marsden and Fuerstenau, 1993).

Today, both of these technologies are well-known in the gold industry, and the choice between carbon adsorption and zinc precipitation depends on several factors that include:

- Precious metal concentration in feed solution,
- Volume of solution that needs to be treated,
- Clarity of solution.

Compared with other recovery processes for gold from cyanide solutions, zinc cementation has the following advantages and disadvantages (Atwood and Atwood, 1985; Miller, 1984; Muhtadi, 1988):

**Advantages:**

- Effective when treating solutions having high silver to gold ratios,
- Fast reaction kinetics,
- Good metal accounting within process,
- Low inventory and capital cost,
- Process easy to operate.

**Disadvantages:**

- Pretreatment of feed solution is required,
- Process is very sensitive to competing ions,
- Dilute solutions will have high zinc consumption as result.

Zinc cementation is primarily used for the recovery of precious metals from highly concentrated solutions, because of the increased zinc consumption per unit precious metals recovered when less concentrated solutions are used. Gold recoveries of 98%, 90%, 83% and 50% were found with the treatment of solutions that contained 30ppm, 5ppm, 3ppm and 1ppm of gold, respectively (Atwood and Atwood, 1985). However, this is not the case with silver recovery, which remain high even at low concentration in the pregnant solution (Atwood and Atwood, 1985). Thus zinc cementation is more favoured for silver recovery from dilute solutions, because of the poor loading of silver on activated carbon. However, gold recovery from dilute solutions are mostly performed by adsorption onto activated carbon, because of the high affinity that activated carbon has for the aurocyanide complex (Hiskey, 1983; Miller, 1984; Muhtadi, 1988).

Information on the recovery of platinum and palladium from cyanide solutions using zinc cementation is limited. The research that has been performed was done on solutions from cyanide leaching of recycled automobile catalyst, for the recovery of platinum, palladium and rhodium. It was concluded that inadequate recovery of these metals was obtained using zinc cementation (Desmond *et al.*, 1991; Sibrell and Atkinson, 1995). Sibrell and Atkinson (1995) found that only 50% of platinum and 10% of rhodium could be recovered with zinc cementation at 60°C. The solution used was very concentrated in platinum and palladium (between 150 ppm and 500 ppm), and thus it is uncertain if the process will be more effective when treating solutions having low concentrations of platinum and palladium.



### 2.2.2 Thermal Hydrolysis

Thermal hydrolysis has been investigated for the recovery of platinum, palladium and rhodium from cyanide solutions resulting from leaching recycled automotive catalyst with cyanide. The process has primarily been performed on laboratory and development scale (Desmond *et al.*, 1991; Kuczynski *et al.*, 1992). In this process pregnant cyanide solution containing platinum, palladium and gold was transferred into autoclaves at temperatures ranging from 200°C to 275°C, without any agitation within the autoclave.

At high temperatures, cyanide is unstable, and decomposes, resulting in the precipitation of the platinum, palladium and rhodium in their metallic state. Table 2.4 shows the results found by Desmond *et al.*(1991) for high temperature treatment of a cyanide leach solution, containing platinum, palladium and rhodium, where the head temperature represents the temperature of the pregnant cyanide leach solution.

**Table 2.4:** Thermal hydrolysis results for platinum, palladium and rhodium at different temperatures (Desmond *et al.*, 1991)

Temp (°C)	Pressure (psig)	Concentration (mg/l)		
		Pt	Pd	Rh
Head	n/a	145	42	14
200	210	146	1.4	12
225	350	102	0.4	5.4
250	600	0.2	> 0.1	> 0.1
275	900	0.4	> 0.1	>0.1

Desmond *et al.*(1991) concluded that in each case, the metal concentration at higher temperatures decreased from a maximum at 160 °C that was used during the leaching. This suggested that the metal complexes that formed at 160 °C were unstable at higher temperatures, which resulted in the decomposition of the metal-cyano complexes and subsequent precipitation of the metals from solution. From Table 2.4 it can be seen that  $Pt(CN)_4^{-2}$  was more thermally stable than  $Pd(CN)_4^{-2}$  and  $Rh(CN)_6^{-3}$ , with the platinum concentration in solution decreasing substantially at temperatures above 225°C. It can, however, be observed that more than 99% of the PGMs were removed from the solution at temperatures of 250°C or higher.

Another important advantage of thermal hydrolysis is the almost complete destruction of the total cyanide in solution during thermal treatment. The free cyanide concentration in the pregnant leach solution was reduced to 0.2 ppm at 225 °C, which is lower than the allowable amount of cyanide in drinking water (Desmond *et al.*, 1991). However, although the solution was safe for disposal when considering the free cyanide and heavy

metal concentrations, dissolved solids, such as  $Na_2CO_3$ , and the high pH of the solution, made disposal of the solution to a public water source or sewer unacceptable.

The main advantages and disadvantages of thermal hydrolysis include:

**Advantages:**

- The process is fast, due to the high temperature used.
- Produces products of high purity.
- Lower free cyanide concentration in effluent to environmental accepted limits.

**Disadvantages:**

- The process can only be used effectively to treat high strength solutions.
- The energy costs associated with the process are high.

From a process standpoint, however, thermal hydrolysis, should be used when the solution strength is high. Thus the use of thermal hydrolysis in the case of this project is not an option for treating the heap leach solution, but should rather be considered for the treatment of the eluate, which will be highly concentrated in platinum, palladium and gold. No effort was made in the studies mentioned to investigate the effect of base metal concentration on the purity of the precipitation product produced during thermal hydrolysis. During the leaching of automobile catalyst, this is not a problem, because of the small amounts of base metals present in the leach solution.

### 2.2.3 Solvent Extraction

The use of solvent extraction for the recovery of gold from cyanide solutions has been investigated by a number of researchers, because of the selective recovery of metals that can be achieved with solvent extraction, when the appropriate carriers are used in the organic phase. Mooiman and Miller (1991), concluded that effective recovery of gold from cyanide solutions could be achieved when tributyl phosphate (TBP) or dibutyl butylphosphonate (DBBP) are used as carriers in the organic phase. However, the solution used in the study had a pH of 8, which is lower than would be expected from a typical cyanide leach liquor. The study also concluded that the mechanism involved during recovery of aurocyanide is similar to the mechanism involved during the adsorption of aurocyanide onto activated carbon.

Kordosky *et al.*(1992) found the guanidine ion pairing functionality to be an effective extractant for gold, from cyanide solutions at a pH above 10. The extractant maintains its protonated form at a pH of approximately 10.5, and also shows gold selectivity over copper and iron in solution.

No studies could be found on the recovery of platinum and palladium from cyanide solutions using solvent extraction. Listed below are some of the main advantages and disadvantages associated with solvent extraction (Kargari *et al.*, 2004; Niu and Volesky, 1999):

#### **Advantages**

- Simple and flexible process, with no complex equipment needed,
- Recovery of metals can be controlled,
- High selectivity can be achieved.

#### **Disadvantages**

- Separation of trace amounts of metals is difficult, because of the low driving force involved, thus pre-concentration is needed,
- Solvent extraction is restricted to clarified solutions,
- Extractants partially soluble in aqueous phase leads to solvent and metal losses,
- Emulsion formation can occur within process.

### **2.2.4 Activated Carbon**

The carbon-in-pulp (CIP) process has been the primary hydrometallurgical option for the recovery of gold from cyanide solutions over the past few decades. The ability of activated carbon to recover gold from chloride solutions was recognized in 1847 and patented in 1880 for the recovery of gold from chloride leach solutions (Davis, 1880). However, it was not until 1894 that the use of activated carbon for the recovery of gold from cyanide leach solutions was patented, and it took another 80 years before activated carbon technology had developed sufficiently as an alternative to zinc cementation.

One of the main factors that enabled activated carbon to become the process of choice for the recovery of gold from cyanide solutions was the fact that the costly solid-liquid separation step associated with zinc cementation could be avoided, since activated carbon could function effectively in pulp solutions. The development of the Zadra process at the United States of America Bureau of Mines for the elution and regeneration of activated carbon, which enabled the carbon to be recycled in the process, was a crucial aspect in the acceptance of the technology commercially (Zadra, 1950, 1952; Van Vliet, 1991).

In the case of activated carbon, however, the engineering aspects associated with the process have been developed more thoroughly than the fundamentals of the chemistry

associated with adsorption onto activated carbon, leading to disagreement among researchers (McDougall *et al.*, 1987; McDougall, 1981, 1980). Theories on the adsorption of aurocyanide onto activated carbon include, (1) the reduction of  $Au(CN)_2^-$  to metallic gold, (2) the adsorption of  $[M^{n+}][Au(CN)_2^-]_n$  ion pairs, (3) electrical double-layer adsorption of  $Au(CN)_2^-$  anions and cations onto a charged surface, (4) ion exchange extraction of  $Au(CN)_2^-$  anions by positively charged carbonium-ion sites, (5) adsorption of  $Au(CN)_2^-$  anions with subsequent degradation to the  $AuCN$  polymeric species and (6) adsorption of ion pairs followed by partial reduction of the  $Au(CN)_2^-$  complex to a cluster-type species (Adams *et al.*, 1987*b*; Jones *et al.*, 1989).

Although there exists some controversy among researchers about the actual mechanism of aurocyanide adsorption onto activated carbon, much research has been performed on the process, regarding equilibrium and kinetic studies, modeling of the process, pilot plant studies and also reviews on commercial CIP and carbon-in-leach (CIL) plants (Adams *et al.*, 1987*a,b*; McDougall *et al.*, 1987; McDougall, 1981, 1980; McDougall *et al.*, 1980; Nicol *et al.*, 1984). In all these studies it was concluded that effective recovery of gold from cyanide solutions was achieved under almost all conditions employed.

Most of the literature available for the recovery of platinum and palladium from cyanide leach solutions using activated carbon report studies performed on the recovery of these metals from hydrochloric acid solutions (Ageeva *et al.*, 2001; Chand *et al.*, 2009; Chen *et al.*, 2007). These studies concluded that effective recovery of platinum and palladium is possible from hydrochloric acid solutions using activated carbon. Very little information is available on the recovery of platinum and palladium from cyanide solutions using activated carbon. Desmond *et al.*(1991) found that 99% of platinum and palladium could be recovered from a pregnant cyanide leach solution that originated from the leaching of recycled automobile catalyst, using activated carbon. However, activated carbon was removed from the study as a process option, because of the low capacity of activated carbon, that resulted in low loadings of both metals.

Compared with ion exchange resins, activated carbon display the following advantages and disadvantages (Fleming, 1993):

#### **Advantages**

- Because of the larger particle size of activated carbon, the pre-screening and interstage screening duties can be performed on screens that are easier to manage industrially,
- Activated carbon is cheaper than commercially available ion exchange resins,
- Because of the slow kinetics of precious metal adsorption onto activated carbon, the CIP plant will operate far from equilibrium.

### **Disadvantages**

- Slow kinetics and low exchange capacity,
- Poisoned by organics, such as humates, flotation reagents, machine oils and solvents,
- Requires periodic regeneration, which will increase the operating cost significantly,
- Major loss of carbon during operation in a typical CIP plant.

# Chapter 3

## Anion Exchange

### 3.1 History

Ion exchange technology for the recovery of valuables from process streams is a relatively new technology, when compared with other hydrometallurgical recovery processes, such as activated carbon and zinc cementation. The technology first became a viable process option with the introduction of synthetic ion exchange polymeric materials, from which resins were first used in a hydrometallurgical process for the recovery of uranium in the 1960's. In the 1970's ion exchange resins found their first application for the recovery of precious metals in the Union of Soviet Social Republics (USSR), for the recovery of gold from cyanide solutions (O'Malley, 2002; Moyer and Singh, 2004). It was not until the 1980's, with the commissioning of the Golden Jubilee Mine in South Africa, that ion exchange resins were first used commercially in the West for the recovery of precious metals. They were used for the recovery of gold (Moyer and Singh, 2004).

Today, large ion exchange resin manufacturing companies exist (eg. Purolite, The Dow Chemical Company) which produce ion exchange resins of all types for applications in the water, waste treatment and mining industries. Commercially, however, ion exchange resins are currently being used to a limited extent in the precious metal industry, because of their higher cost, smaller particle size and poor selectivity with respect to base metals, compared to activated carbon (O'Malley, 2002). Research companies such as Mintek have investigated the application of ion exchange resins in the precious metal industry, which led to the synthesis of the gold-selective resin, Minix (Van Deventer *et al.*, 1999).

Anion exchange resins, however, are superior to activated carbon, when considering loading kinetics and exchange capacity. Other advantages of anion exchange resins include their ability to be eluted at room temperature, the ability to be modified to be selective, resistance to poisoning by organic species and the fact that no thermal regeneration is required (Fleming and Cromberge, 1984*b,c*; Kotze *et al.*, 2005; Lewis and Bouwer, 2000;

Petersen and van Deventer, 1997).

The industrial use of anion exchange resins for precious metal recovery from cyanide solutions are, however, limited to the recovery of gold and silver, probably because these two precious metals have been recovered using cyanide for decades. It was not until recently that researchers have started to investigate the recovery of platinum and palladium, in most cases from recycled automotive catalytic converters, using cyanide as leaching agent. Some of these investigations were then followed by proposals and investigations into possible downstream processes for the recovery of the dissolved platinum group metals (PGMs) from cyanide solutions, which included using ion exchange resins (Allison and Thompson, 1992; Bax, 2008; Cortina *et al.*, 1998; Roijals *et al.*, 1996; Shams *et al.*, 2004). The information currently available on PGM-cyanides, and their recovery using anion exchange resins, is limited, and much on the subject is still not well-understood.

## 3.2 Structure, Syntheses and Physical Properties of Anion Exchange Resins

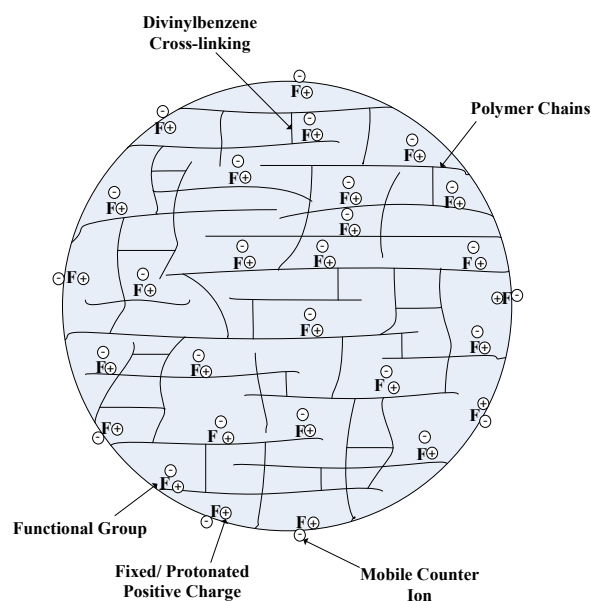


Figure 3.1: Schematic of an anion exchange resin

Modern anion exchange resins consist of spherical, inert hydrocarbon matrices, to which charged functional groups are attached by covalent bonding (Dicinoski, 1994). The matrices consist of a polymer that is either polystyrene or acrylic and that is cross-linked with divinylbenzene to provide structural stability. The polymer used in the matrix and the degree of cross-linking determines the physical properties of the resin, whereas the

functional groups attached to the matrix determine the selectivity and type of exchange reaction that will take place. The exchangeable anions on the resin that will exchange with the anions in the surrounding environment are bound to the functional groups on the resin matrix, and are usually chloride, bisulphide or hydroxide ions. They are selected so that the affinity of the resin is much lower for them than for the anions contained in the solution. Figure 3.1 represents a schematic of a typical anion exchange resin.

### 3.3 Applicability of Different Anion Exchangers

Different types of resins, namely weak-, moderate- and strong-base anion exchange resins, as well as chelating resins, are available for the recovery of anions from solutions. The applicability of these resins for the treatment of specific solutions is, however, strongly dependent on the pH of the solution, as well as the structure and oxidation state of the anions present in the solution. Weak- and moderate-base anion exchange resins contain primary, secondary and tertiary amines as functional groups that need to be protonated, before they can react with anions in solutions. The greater the number of protonated groups on these resins, the higher the potential exchange capacity of the resins. Introducing these protonated resins to a strong alkaline solution will, however, result in the conversion of the protonated groups to their free base form, which will cause the anion exchange capacity to be reduced. This is why these resins typically have pKa values, i.e. the pH where 50% of the functional group on the resin are protonated, between 7 and 9. Thus, for the exchange capacity of weak base resins to be utilized effectively, they must be used in solutions having a pH of between 7 and 9. This restriction on the one hand makes it difficult for weak base resins to be used in cyanide leach solutions, because of the high pH ( $>10.0$ ) associated with these solutions.

Strong base anionic resins on the other hand, can be used effectively in high pH solutions. The fixed protonated sites associated with the quaternary amine functionalities of these resins enables the resin to be stable and effective at any pH. The anion exchange capacities of most strong base resins are much higher than the capacities associated with most weak base anionic resins, which will allow the uptake of high amounts of anions from solution per quantity of resin. However, the disadvantages associated with strong base resins are that they are not as selective as weak base anionic resins, because of their high anion exchange capacity, and the removal of anions from the resins is more complicated.



### 3.4 Equilibrium Loading Models

Equilibrium models are used to predict the loading of single component anion systems onto anion exchange resins. Firstly, an isotherm is generated for each anion in solution, by contacting different amounts of resin with the same amount of solution containing the anion being investigated. Isotherms represent all possible experimental conditions of a given system at a constant temperature. Equilibrium isotherm models that have been used extensively throughout literature to describe the equilibrium loading of aurocyanide ( $Au(CN)_2^-$ ) onto both activated carbon and anion exchange resins are the Freundlich and Langmuir isotherm models, shown in Equations (3.4.1) and (3.4.2), respectively (Van Deventer *et al.*, 1999; Woollacott *et al.*, 1990).

$$Q_e = AC_e^n \quad (3.4.1)$$

$$Q_e = \frac{Q_m BC_e}{1 + BC_e} \quad (3.4.2)$$

where  $Q_e$  in both equations is equal to the loading of a metal on the resin at equilibrium (mg/l). For the Freundlich isotherm in Equation 3.4.1,  $C_e$  is equal to the metal concentration in solution at equilibrium (mg/l), while  $A$  and  $n$  are constants.  $A$  is a function of the energy of adsorption and temperature and a measure of adsorption capacity while  $n$  is a measure of adsorption intensity (Okeola and Odebunmi, 2010). For the Langmuir isotherm in Equation 3.4.2,  $C_e$  is equal to the metal concentration in solution at equilibrium (mg/l),  $Q_m$  is equal to the maximum adsorption of a specific metal (mg/l) and  $B$  is a constant that is related to the adsorption energy (Misak, 1993).

The Freundlich equilibrium model is an empirical model that is mostly used for modelling gold loading onto either activated carbon or ion exchange resins (Lukey *et al.*, 2000b; Sheintuch, 1981). In most cases it provides a better prediction of the data. However, the model does not provide information such as maximum loading, as is the case with the Langmuir isotherm. The Langmuir equilibrium model is a fundamental model which best predicts equilibrium loading when the metal loading is high on the adsorbent. Both these models, however, were specifically developed for modelling single component systems, and not multicomponent systems.

Efforts have been made, by modification of the Freundlich and Langmuir isotherm models, to develop equilibrium models that could predict multicomponent systems (Lukey *et al.*, 2000b; Misak, 1993; Sheintuch, 1981). The prediction of multicomponent equilibrium is, however, a rigorous process, because the equilibrium loading of a single anion will be affected by several factors such as competition from other anions in solution, the different affinities of the resin for different anions, and the concentration of the different anions

in solution. Thus, to acquire a multicomponent isotherm requires a extensive amount of experimentation, because the equilibrium loading of each anion is now a function of the concentrations of all anions in solution. This means that a large number of experiments need to be performed in order to obtain the functional relationships between all the anions in solution.

### 3.5 Kinetics of Loading

In studies performed on the recovery of aurocyanide by ion exchange resins, it was concluded that the rate of adsorption is controlled by film-diffusion in the initial stages of recovery. However, as the resin approaches equilibrium, the rate of adsorption is controlled by both film- and intra-particle diffusion (Kotze *et al.*, 2005). In a study performed by Fleming *et al.*(1984), the effect of agitation within the RIP adsorption tank was investigated, to enable the identification of areas where film-diffusion control or intra-particle -diffusion control were dominant, and as a result the following guidelines were developed:

- In processes where the rate is controlled by film-diffusion, the rate of adsorption can be improved by improving the mixing efficiency, whereas under intra-particle control the mixing has no effect on the rate of adsorption.
- Under film-diffusion control, the rate has a first-order dependence on the metal concentration in solution, whereas under intra-particle diffusion this dependence is less than first order.
- The pH of the solution will have a minimal effect on the rate of adsorption under conditions of film-diffusion, but could have a significant effect on the rate of adsorption under conditions of intra-particle diffusion.

For film-diffusion controlled conditions the rate of aurocyanide loading is inversely proportional to the mean diameter of the resin beads, thus the smaller the beads, the faster the loading of gold. As the resin becomes loaded, and conditions of intra-particle control are entered, the rate of adsorption becomes inversely proportional to the square of the mean diameter of the resin beads (Kotze *et al.*, 2005).

### 3.6 Selectivity Aspects

Anion exchange resins do not adsorb all anions in solution equally. Selectivity or preference of an anion exchange resin for one anion over another can be measured by the relative affinity that the resin exhibits for different anions in solution. Selectivity can be

expressed quantitatively, as a distribution coefficient,  $K_i$ , or as a separation factor,  $\alpha_{ij}$ , as defined in equations (3.6.1) and (3.6.2), respectively.

$$K_i = \frac{C_{i,r}}{C_{i,s}} \quad (3.6.1)$$

$$\alpha_{i,j} = \frac{K_i}{K_j} \quad (3.6.2)$$

The distribution coefficient is described by the ratio between the concentration of species  $i$ , in the resin phase,  $C_{i,r}$ , and in the solution phase,  $C_{i,s}$ , at equilibrium, whereas the separation factor is described as the ratio between two different species distribution coefficients. From equations (3.6.1) and (3.6.2), it is clear that a resin will have the greatest affinity for the species with the highest distribution coefficient, or separation factor, relative to the other species present in solution.

Ideally it would be desirable to modify anion exchange resins to be selective towards certain anions in a specific solution. Selectivity, however, is a complex subject, because it is a function of solution properties, properties of competing anions, type of resin, resin structure and resin functionality (Aveston *et al.*, 1958; Barron and Fritz, 1984; Christopher *et al.*, 1997; Gjerde and Fritz, 1979; Riveros, 1993; Tetsuo, 1997; Versiane and Ciminelli, 2000). All of these factors will contribute in the selection process of an anion exchange resin for a specific process.

### 3.6.1 Solution Properties

Properties of the solution to be treated, such as the concentration of the different anions, pH, temperature and free cyanide concentration, will have an effect on the adsorption. The adsorption of anions dilute in solution will be affected by anions having higher concentrations. Low concentrations, will reduce the probability of anions interacting with active sites on the resin, when in solution with a variety of other anionic species.

The effects of solution pH on the applicability of different anion exchangers for specific solutions were discussed in Section 3.3. The anion exchange capacity of weak base resins will be reduced dramatically when used in solutions having a high pH. However, low anion exchange capacity is not necessarily a negative resin characteristic, when selective adsorption of certain anions are considered, as will be discussed in Section 3.6.3.

The anion exchange reaction between the active sites and anions in solution is known to be slightly exothermic (Dicinoski, 1994; Fleming and Cromberge, 1984*b*). Thus it can be expected that the high temperature (up to 60°C) of the solution in this investigation will have an effect on the loading of anions onto the anion exchange resins, because of the exothermic exchange reaction. The effect of temperature on the loading of anion exchange

resins is, however, small compared with the effect of temperature on the loading of anions onto activated carbon (Fleming and Cromberge, 1984b). However, when considering the Arrhenius equation,  $k = A \exp(\frac{-E_a}{RT})$ , it can be expected that the loading rate constant,  $k$ , of the anions will increase with increasing temperature. The decrease in loading should thus be played off against the increase in loading rate, when evaluating the feasibility of a high temperature adsorption process.

It should be noted that although the solution properties will have a pronounced effect on the loading of anion exchange resins, it will, in most cases, be difficult to change these properties. Mostly the solutions come from upstream processes, in which the properties were optimally selected for that specific goal, and changes to these solution properties cannot be made easily.

### 3.6.2 Type of Anions

Selective adsorption of anions by anion exchange resins is influenced primarily by the charge and polarizability of the anions, and to a lesser extent by the shape and size of the anions (Aveston *et al.*, 1958). Table 3.1 shows the most likely metal-cyano complexes to be encountered in the cyanide heap leach solution being investigated, along with their structures, degree of hydration and stability constants (Aveston *et al.*, 1958; Christison, 2003; Dicoski, 1994). Where the stability constant,  $\beta$ , is defined as the ratio of the concentration of the metal-ligand to the product of the concentrations of the metal and the ligand.

**Table 3.1:** Properties of primary metal anions in solution

Anion	Structure	Degree of Hydration	Stability ( $\text{Log}\beta$ )	Type of Complex
$Au(CN)_2^-$	Linear	Low	47	Strong
$Pt(CN)_4^{-2}$	Square-planar	Medium	40	Strong
$Pd(CN)_4^{-2}$	Square-planar	Medium	42.4	Strong
$Cu(CN)_2^-$	Linear	Low	22	Weak
$Cu(CN)_3^{-2}$	Trigonal planar or Trigonal bipyramidal	Medium	27	Weak
$Cu(CN)_4^{-3}$	Tetrahedral	High	28	Weak
$Ni(CN)_4^{-2}$	Square-planar	Medium	30	Weak
$Zn(CN)_4^{2-}$	Tetrahedral	Medium	17	Weak
$Fe(CN)_6^{-4}$	Octahedral	High	35	Strong

The charge of an anion will determine how many counter ions on the resin need to be displaced for that anion to adsorb. Adsorption of multi-valent anions like  $Fe(CN)_6^{-4}$  will require four quaternary ammonium groups, spaced closely enough together to compensate for the four negative charges of the anion. Monovalent anions, such as  $Au(CN)_2^-$  and  $Cu(CN)_2^-$ , will require one quaternary ammonium group, with no spacing restrictions between different active sites. Thus selective adsorption of different anions will depend strongly on the configuration of quaternary ammonium groups, which is directly related to the ionic density (exchange capacity) of the resins (Barron and Fritz, 1984; Riveros, 1993; Versiane and Ciminelli, 2000).

The degree of hydration of an anionic complex in solution will determine the compatibility of that complex with a certain resin matrix. The hydration of anionic complexes depends on the charge density of the complex, meaning the ratio of charge to number of elements in the complex. The higher the ratio, the more water molecules are required to stabilize the anion in solution, and thus the more hydrated the complex (Cortina *et al.*, 1998; Versiane and Ciminelli, 2000). For example, the low charge density of  $Au(CN)_2^-$  (1 negative charge in 5 atoms), explains its hydrophobic character, and provides one reason why the less hydrated carbon has a high affinity for the aurocyanide anion. On the other hand, anions with a high charge density, such as  $Cu(CN)_4^{-3}$  (3 negative charges in 9 atoms) and  $Fe(CN)_6^{-4}$  (4 negative charges in 13 atoms), will be more hydrated, and thus be more compatible with an adsorbent with hydrophilic characteristics.

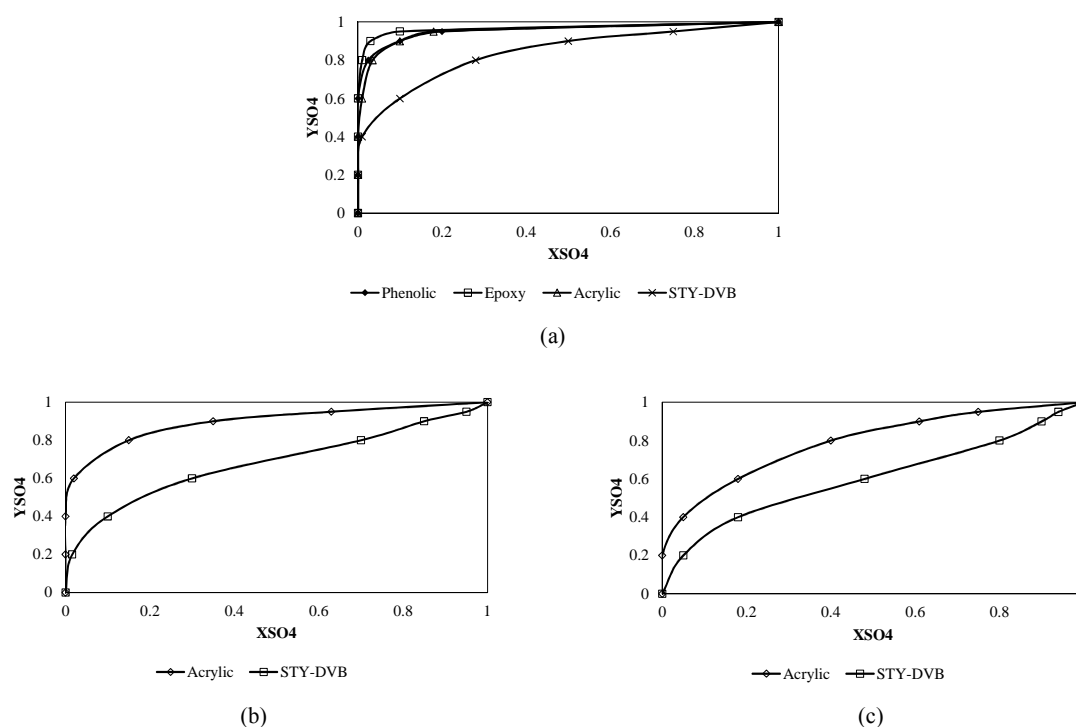
### 3.6.3 Resin Type, Capacity and Structure

Selective adsorption of anions from a solution is affected by the type of resin used. As discussed in Section 3.3, weak base resins will have a much lower exchange capacity than strong base resins. The exchange capacity of weak base resins will also be decreased with an increasing solution pH, because of the conversion of protonated sites to their free base form. Some studies, however, indicated that the use of weak- and moderate base resins resulted in the selective recovery of aurocyanide  $Au(CN)_2^-$  anion over other metal cyanide anions (Fleming and Cromberge, 1984*b*; Green, 1988; Harris *et al.*, 1992; Jermakowicz-Bartkowiak and Kolarz, 2002). It was concluded that the low exchange capacity of these resins could not accommodate the multiple charges of other metals cyanide anions such as  $Cu(CN)_4^{-3}$  and  $Fe(CN)_6^{-4}$ , but they could adsorb the monovalent  $Au(CN)_2^-$  anion, with ease. Thus, low ionic density resins, although having low anion exchange capacities, can be used to recover monovalent anions selectively over multi-valent anions in solution.

Strong base anionic resins, on the other hand, having high exchange capacities, especially the ones containing tri-methyl functionalities, have been found to adsorb anions non-selectively (Aveston *et al.*, 1958; Fleming and Cromberge, 1984*b,c*; Green, 1988; Riveros,

1993; Versiane and Ciminelli, 2000). The reason for this is that the high anion exchange capacity of these resins allows the loading of all anions, low and highly charged. However it was concluded that these resins had greater affinity towards highly charged anions such as  $Cu(CN)_4^{-3}$  and  $Fe(CN)_6^{-4}$ , than towards monovalent anions such as  $Au(CN)_2^-$  and  $Ag(CN)_2^-$  (Aveston *et al.*, 1958). To overcome this non-selective adsorption of strong base resins, it was proposed that the resin capacity be decreased. This will result in the active sites being spaced far from each other on the resin matrix, making the adsorption of multivalent anions difficult (Aveston *et al.*, 1958). Decreasing the exchange capacity of strong base anionic resins to make them more selective was one of the principles used in the development of the gold-selective resin, Minix (Kotze *et al.*, 2005).

The resin matrix will also influence the selectivity of anion exchange resins. Clifford and Weber (1983) investigated the factors that would affect divalent/monovalent selectivity in anion exchangers, using a binary solution of sulphate( $SO_4^{2-}$ ) and nitrate( $NO_3^-$ ). The isotherm results generated for different types of anion exchange resins consisting of different matrices are presented in Figure 3.2 (a-c), where Y represents the fraction of species on the resin and X the fraction of species in solution.



**Figure 3.2:** The effect of divalent/monovalent ( $SO_4^{2-}/NO_3^-$ ) selectivity of (a) polyamine, (b) tertiary amine and (c) quaternary amine resins (Clifford and Weber, 1983)

The anion exchange resins containing polyamine and tertiary amine functionalities in Figure 3.2 (a) and (b), were weak- and moderate base anionic exchangers respectively,

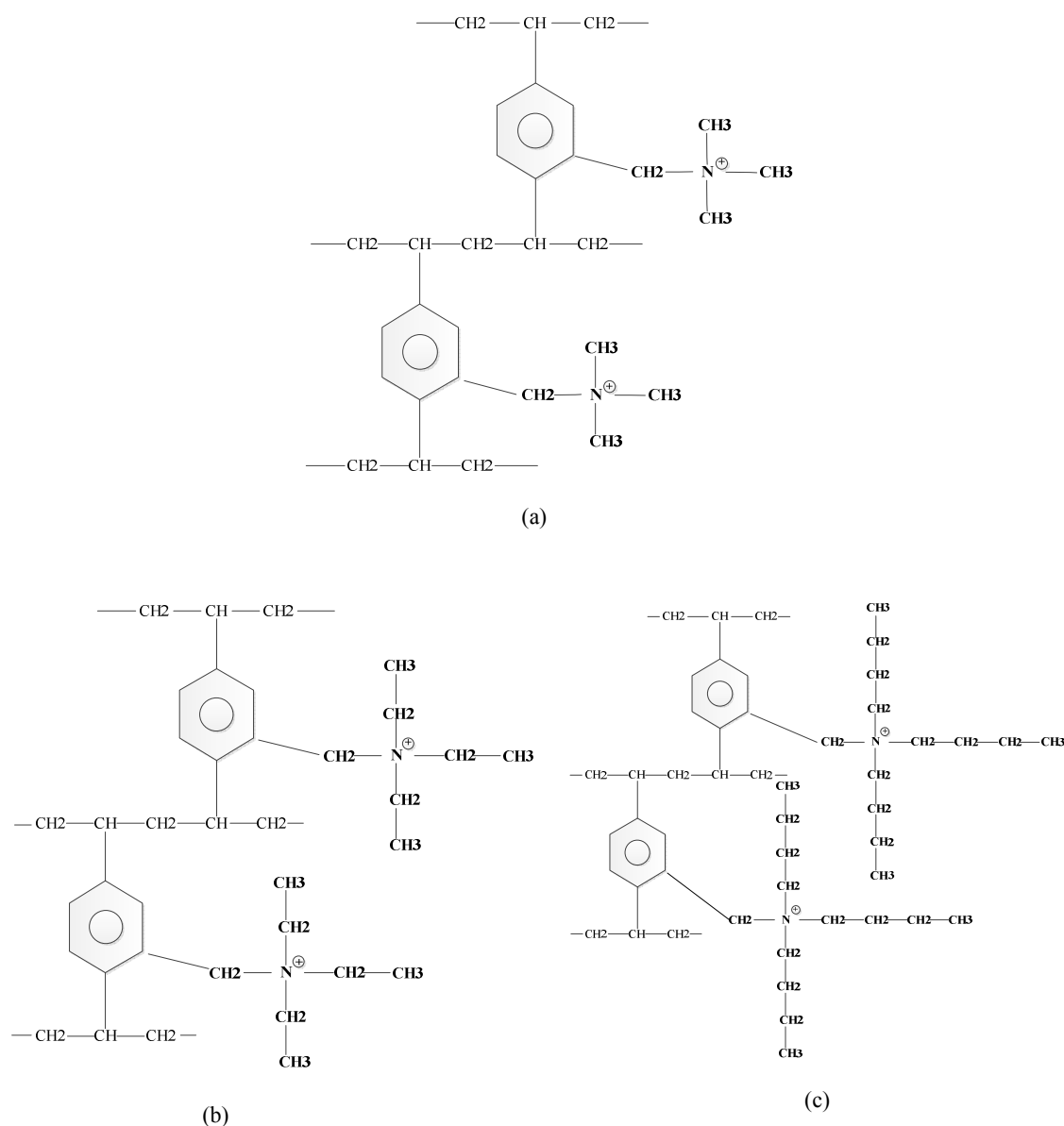
whereas the resin containing quaternary amine functionality in Figure 3.2 (c) was a strong base anion exchanger. The anion exchange resin containing polyamine functionality in Figure 3.2 (a), in reality contained a mixture of primary, secondary and tertiary amines, and is therefore classified as polyamine (Clifford and Weber, 1983).

From Figure 3.2, it can be seen that anion exchangers containing epoxy, phenolic and acrylic matrices, had a higher affinity for the divalent ( $SO_4^{2-}$ ) over the monovalent anion ( $NO_3^-$ ), whereas anion exchangers containing styrene-divinylbenzene (STY-DVB) matrices had a higher affinity for the monovalent anion over the divalent anion. The latter was true for all cases, despite the different functionalities of the anion exchangers. This confirmed the conclusions of other researchers (Riveros, 1993; Versiane and Ciminelli, 2000), that selectivity of anion exchange resins is a function of the hydrophilicity of the resin matrix. The polystyrene-divinylbenzene matrices provide anion exchange resins with a hydrophobic character, because hydrogen bonds between water and the polystyrene matrix cannot be well established (Riveros, 1993). On the other hand, matrices consisting for example of polyacrylics, provide anion exchange resins with a hydrophilic character, because they consist of carbonyl and secondary amine groups which allow hydrogen bonds with water and solvated ions (Riveros, 1993; Versiane and Ciminelli, 2000). As discussed in Section 3.6.2, some anions will be more hydrated than others, giving them a hydrophilic or hydrophobic character. Less hydrated anions such as  $Au(CN)_2^-$  and  $Ag(CN)_2^-$ , will thus show higher affinity for the hydrophobic polystyrene resins, whereas more hydrated anions such as  $Cu(CN)_4^{-3}$  and  $Fe(CN)_6^{-4}$ , will show higher affinity for the hydrophilic polyacrylic resins.

### 3.6.4 Resin Functionality

When using strong base anion exchange resins, the functional groups on these resins play an important role in creating an environment for non-selective adsorption. Using larger rather than smaller functional groups will increase the selectivity of anion exchange resins for lower-charged anions over higher charged anions. Figure 3.3 shows three strong base resins containing different quaternary ammonium groups namely, tri-methyl, tri-ethyl and tri-butyl.

Studies performed on anion exchange selectivity concluded that selectivity is dependent on the configuration of the quaternary ammonium groups on the anion exchanger (Riveros, 1993; Versiane and Ciminelli, 2000). When considering the tri-methyl functionality of the strong base resin in Figure 3.3 (a), it was concluded that adsorption of anions onto this type of resin was non-selective (Aveston *et al.*, 1958; Fleming and Cromberge, 1984*b,c*; Green, 1988; Riveros, 1993; Versiane and Ciminelli, 2000). In contrast it was observed that strong base resins containing tri-ethyl functionalities and tri-butyl func-



**Figure 3.3:** Strong base anionic resins containing different functionalities - (a) tri-methyl ammonium, (b) tri-ethyl ammonium and (c) tri-butyl ammonium

functionalities in Figure 3.3 (a) and (b), showed higher affinities for divalent metal cyanide anions, such as  $Ni(CN)_4^{-2}$  and  $Zn(CN)_4^{-2}$ , and monovalent metal cyanide anions, such as  $Au(CN)_2^-$  and  $Ag(CN)_2^-$ , respectively (Riveros, 1993; Van Deventer *et al.*, 1999; Versiane and Ciminelli, 2000).

The fact that smaller functional groups show non-selective adsorption, whereas larger functional groups have higher affinities for lower charged anions, can be explained by a stereochemical effect imposed by the functional group during the adsorption process. When considering a highly charged anion such as  $Fe(CN)_6^{-4}$ , four quaternary ammonium groups, spaced closely together, will be required to adsorb. The adsorption of this anion will be hindered by the rotational restrictions imposed by an alkyl chain longer than a



methyl group, such as tri-ethyl or tri-butyl groups. The adsorption of divalent anions such as those of  $Ni(CN)_4^{-2}$  and  $Zn(CN)_4^{-2}$ , which requires only two ammonium groups will not be hindered to a noticeable extent by larger functional groups. Thus functionality of resins can be used to selectively recover certain anions over other anions in a solution.

### 3.7 Summary of the findings of studies performed on the recovery of precious and platinum group metals from cyanide solutions

As already mentioned, a considerable number of studies have been performed on the recovery of gold from cyanide solutions with the use of ion exchange resins. Studies performed on the recovery of gold from cyanide solutions on both laboratory and pilot-plant scale suggest that both strong and weak base resins can be used to recover aurocyanide (Fleming and Cromberge, 1984*b,c*). However, there is a preference among researchers to use strong base resins, because of the higher loadings that can be obtained, and also the lower cost of strong base anionic resins compared to weak base anionic resins. The problem with strong base resins, however, is the fact that considerable amounts of base metals are co-extracted with the gold onto the strong base resins, making the subsequent elution process technically complex (Fleming and Cromberge, 1984*b,c*; Kwak *et al.*, 2010; Versiane and Ciminelli, 2000).

Mintek developed a gold-selective resin, Minix, that can be used to recover gold from either low or high grade cyanide solutions, selectively over other metal-cyanides present in solution (Kotze *et al.*, 2005; Van Deventer *et al.*, 1999). Mintek recognized that altering the properties of anions present in the solution to the extent that commercially available resins will be more selective towards aurocyanide will be difficult, and that the resin structure should rather be modified to serve this purpose. Aveston *et al.*(1958) found that increasing the average distance between positive resin sites decreased the affinity of the resin for multi-charged metal cyanide anions. This could be achieved by using two approaches (Kotze *et al.*, 2005):

- Lowering the functional group structure, thus in effect the exchange capacity of the resin. This was the basis used in the development of Minix.
- Using a combination of secondary and tertiary amines during the functionalization of the resin. This will increase the distance between active sites and the secondary amines will be in their free base form in solutions having a high pH, resulting in a lower exchange capacity.

The lowering of the exchange capacity to increase the affinity of resins for single-charged anions, and lowering their affinity for multi-charged anions, was confirmed by Clifford and Weber (1983). Riveros (1993), on the other hand found that the size of the functional groups on strong base resins played an important role in their affinity for aurocyanide. The larger the functional group, the more selective the resin became for lower charged metal cyanide anions. The reason for this is the fact that adsorption of multi-charged anions is hindered by the sterical effect imposed by the larger functional groups on the resin (Riveros, 1993). It can be concluded that the recovery of gold from cyanide solutions with the use of ion exchange resins is well-understood and thoroughly studied.

Information on the recovery of platinum and palladium from cyanide solutions is scarce and only comprises qualitative discussions. Cortina *et al.*(1998) concluded that effective recovery of PGM-cyanide complexes could be achieved with the use of strong base anionic resins. Similar results were found in studies performed by Roijals *et al.*(1996), Shams *et al.* and Desmond *et al.*. The problem with these studies is that they were all performed on cyanide solutions obtained from leaching recycled automobile catalyst with cyanide. The concentration of platinum and palladium in the solutions used in the studies ranged from 150ppm to 500ppm, without significant amounts of base metals. This is not the case in cyanide heap leach solutions, where it can be expected that the concentration of valuable metals will be much lower, with significant amounts of base metals. Thus although these studies confirmed the recovery of PGMs from cyanide solutions with ion exchange resins, they can only be used as a basis for this study, because of the difference in solution chemistry of heap leach solutions.

### 3.8 Elution and Regeneration

Removal of the metal cyanide complexes from anion exchange resins is complex, and probably the most important aspect of the entire process. This is where the solution is produced that will be sent directly to the refining process. Conradie *et al.* (1995) specified essential and desirable criteria for an effective elution process, namely:

**Essential Criteria:**

- The metals of interest must be eluted from the resin to concentrations of less than 50 mg/kg. This will eliminate rapid loss of exchange capacity, and thus ensure low concentrations of these metals in solution, in the adsorption stage.
- The resins must be able to convert back to their original form.

- There must be a suitable and effective process for the recovery of metals from the eluate.
- Cost effectiveness of the elution process must be a priority.

**Desirable Criteria:**

- The elution kinetics should be fast. This will decrease the size of the elution plant, and also minimize the lock-up of metals and resins in the elution circuit.
- A simple elution process would be desirable.

With the attention shifting over the past three decades towards ion exchange as an alternative process option for the recovery of gold from cyanide solutions, as opposed to activated carbon, a considerable amount of research has been done on the elution of aurocyanide from many types of resins (Conradie *et al.*, 1995; Dicoski, 1994; Fleming and Cromberge, 1984*c,a*; Lukey *et al.*, 2000*a*; Oliveria *et al.*, 2008; Staker and Sandberg, 1997). However no studies or reports could be found on the elution of platinum and palladium cyanide complexes from anion exchange resins. With this in mind, aurocyanide elution can be used as a basis for the elution of platinum cyanide and palladium cyanide from ion exchange resins.

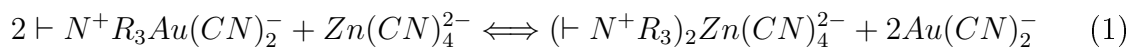
### 3.8.1 Different elution methods

The most common eluants used for eluting aurocyanide from anion exchange resins are acidic thiourea, zinc cyanide and thiocyanate. Two kinds of elution mechanisms are possible, namely chemical and physical elution. Acidic thiourea involves chemical elution, which means that it alters the aurocyanide complex loaded on the resin, in such a way that it can no longer be attached to the anion exchange resin. Zinc cyanide and thiocyanate impose a physical elution mechanism, which means that the adsorbed metal cyanide complexes are physically displaced by either zinc cyanide or thiocyanate anions.

Elution of aurocyanide from anion exchange resins with these three eluting agents are discussed in detail below. With the detailed background on these elution methods, it is hypothesized that platinum and palladium cyanide complexes can be eluted with similar eluting procedures followed during aurocyanide elution.

#### Zinc Cyanide ( $ZnCN_4^{2-}$ )

The elution of aurocyanide from a typical strong base anion exchange resin using zinc cyanide is described below by Reaction 1.

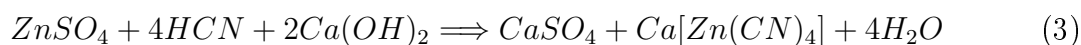


The elution of aurocyanide using zinc cyanide as eluting agent was first proposed by Hazen et al. (1957). The elution process was performed in conjunction with zinc cementation. The elution and cementation were performed as a continuous process, from which the zinc cyanide produced during the cementation eluted the aurocyanide from the anion exchange resin, and zinc cementation was used to recover gold from the eluate. This process was found to be ineffective (Fleming and Cromberge, 1984a), and as a result electrowinning is now used to recover gold from the eluate during continuous elution cycles (Conradie *et al.*, 1995).

When using zinc cyanide as eluting agent the zinc cyanide anion displaces the adsorbed metal cyanide anions on the resin. This displacement of metal cyanide anions results in the strong loading of zinc cyanide anions on the resin. Thus the resin needs to be regenerated, removing most of the zinc cyanide from the resin, before the resin is returned to the adsorption process. If the zinc cyanide is not removed before the resin is returned to the adsorption circuit, a major decrease in metal recovery, because of a loss in resin exchange capacity, due to the loaded zinc cyanide will be observed. The most common method to regenerate the resin is using a dilute mineral acid, as indicated in Reaction 2 (Dicinoski, 1994; Fleming and Cromberge, 1984a; Fleming, 1998).



The zinc sulphate and hydrocyanic acid produced during Reaction 2 can be recycled to an alkaline solution, to again produce zinc cyanide to be recycled to the elution circuit, as illustrated in Reaction 3.



Fleming *et al.* (1984) found that 99% of the aurocyanide loaded onto a strong base anionic resin could be eluted within 24 hours, using zinc cyanide as eluant, in an electro-elution experimental set-up. The results in the study indicated that zinc cyanide concentration had little effect on the elution rate and electrowinning efficiency above a concentration of 0.15 M. The elution was performed at 50°C to avoid crystallization of  $Na_2[Zn(CN)_4]$ , which readily occurs at room temperature from solutions containing more

than 0.5M of zinc cyanide, and it was thought that concentration would have a larger effect on the rate of elution at lower temperatures (Fleming and Cromberge, 1984a).

On the basis of Reaction 2, three mol sulphuric acid is required, to remove one mol zinc cyanide from the eluted resin. It was found that a slight excess of sulphuric acid, with respect to this ratio, was required to reduce the concentration of zinc cyanide on the resin to below 1000 g/ ton (Fleming and Cromberge, 1984a).

With respect to base metal elution, zinc cyanide was found to be superior to thiocyanate and acidic thiourea (Fleming and Cromberge, 1984c,a). Zinc cyanide was able to reduce the concentration of all base metals by 85% on the resin, during pilot plant operation (Fleming and Cromberge, 1984c), with no accumulation of any metals during continuous adsorption-elution cycles.

Advantages and disadvantages of using zinc cyanide as eluting agent, during the elution of aurocyanide from strong base resins, include (Conradie *et al.*, 1995; Dicoski, 1994; Fleming and Cromberge, 1984c,a; Fleming, 1998):

**Advantages:**

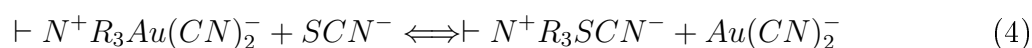
- All metals can be eluted effectively,
- Elution and regeneration chemicals are recyclable,
- Chemicals are not corrosive, thus there are no problems with materials of construction,
- Resin can be regenerated to full capacity.

**Disadvantages:**

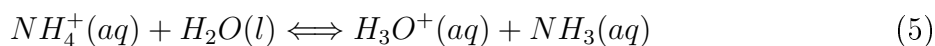
- Regeneration is necessary,
- Chemical consumption can be high,
- Zinc cyanide elution is ineffective when using gold-selective resins,
- Elution kinetics are slow,
- Hydrocyanic gas is produced during regeneration.

**Thiocyanate ( $SCN^-$ )**

The elution of aurocyanide from a strong base resin using thiocyanate has been investigated by several researchers (Fleming and Cromberge, 1984a,c; Lukey *et al.*, 2000a; Oliveria *et al.*, 2008) and is shown in Reaction 4:



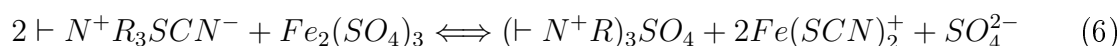
Thiocyanate can be introduced into solution using one of two salts, ammonium thiocyanate ( $NH_4SCN$ ) or potassium thiocyanate ( $KSCN$ ). A study by Lukey *et al.* (2000a) found that the elution of zinc cyanide and iron cyanide, using ammonium thiocyanate, from the strong base resin, Amberjet 4400, was insufficient with less than 40% of either of these metal cyanides eluted. It was concluded that ammonium thiocyanate is not a suitable eluant for strong base resins loaded with large amounts of iron and zinc. The reason for this is the formation and precipitation of double metal complexes such as  $Zn_2(Fe(CN)_6)$  and  $Fe_4(Fe(CN)_6)_3$ , in low pH solutions (Lukey *et al.*, 2000a). Although the solution at the start of the elution is approximately at pH 7, the pH starts to decrease because of the rapid formation of the hydronium ion in solution, as shown in Reaction 5, causing the double metal complexes of iron and zinc to precipitate (Lukey *et al.*, 2000a).



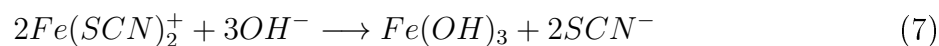
This finding is contrary to the finding of Fleming and Cromberge (1984), who found that ammonium thiocyanate effectively eluted aurocyanide from strong base resins. It should, however, be noted that in this study the resin was only loaded with aurocyanide and no zinc cyanide and iron cyanide were present on the resin.

The use of potassium thiocyanate eliminates this problem, because the salt is soluble in a alkaline solution, typically having a pH equal to or higher than 12, without having reactions that will lower the pH during operation. In these strong alkaline solutions, the double metal complexes of zinc and iron are soluble. It was found that more than 95% of the iron copper and gold could be eluted from strong base resins, with the use of potassium thiocyanate (Lukey *et al.*, 2000a).

Regeneration of strong base resins after elution can be performed using a ferric salt, a method that was developed by Mintek (Fleming, 1998; Fleming and Cromberge, 1984a). The ferric ions react with the thiocyanate loaded on the resin, forming cationic complexes, such as  $FeSCN^{2+}$  and  $Fe(SCN)_2^+$ , which are readily displaced from the resin, as shown in Reaction 6.



Thiocyanate can then be recovered from the solution, via the precipitation of iron, as ferric hydroxide, as shown in Reaction 7. The ferric hydroxide precipitate can be dissolved in an acid solution and be recycled back to the regeneration process.



Elution with thiocyanate has not been used commercially, and has only been tested on laboratory scale. The main reasons for this is the complexity of the elution, and the fact that studies indicated that the efficiency of the regeneration decreased when the same ferric solution was used in continuous elution-regeneration cycles (Fleming, 1998; Fleming and Cromberge, 1984a). Other solutions for the regeneration of strong base resins loaded with thiocyanate have been investigated and include nitric acid, hydrochloric acid, sodium cyanide, sodium hydroxide and sulphuric acid (Fleming and Cromberge, 1984a). However, due to the difficult displacement of thiocyanate from strong base resins, all these solutions indicated insufficient removal of thiocyanate from strong base resins.

Advantages and disadvantages of using thiocyanate as eluting agent, during the elution of aurocyanide from strong base resins, include (Fleming and Cromberge, 1984a; Dicoski, 1994):

**Advantages:**

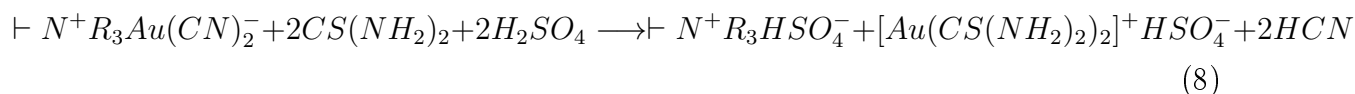
- Fast and effective elution of all metal cyanides,
- Resin can be regenerated to full capacity with recycling of reagents within the elution process,
- Elution chemicals are not toxic or corrosive.

**Disadvantages:**

- Regeneration of resin is required,
- Effective regenerant not found yet,
- Chemical consumption can be high.

**Acidic Thiourea ( $CS(NH_2)_2$ )**

The two elution methods described previously are deemed to be physical elutions. An alternative to these methods is chemical elution with acidic thiourea. Acidic thiourea strips gold from strong base resins by converting the aurocyanide anion to the cationic aurous thiourea complex, as shown in Reaction 8 (Fleming and Cromberge, 1984a; Fleming, 1998):



Either hydrochloric acid or sulphuric acid can be used in this elution method, depending on the desired form that the resin has to be in after elution. The advantage of eluting with acidic thiourea is that the resin is converted to a form that can be used again directly for adsorption, and thus theoretically no regeneration is required (Conradie *et al.*, 1995; Fleming, 1998; Fleming and Cromberge, 1984*a*).

The main disadvantage of this eluting method is that in cases where large amounts of base metal cyanide anions are co-extracted with aurocyanide, they are poorly eluted with acidic thiourea, which results in multi-elution techniques being needed for an effective elution process. The problem is particularly serious when large amounts of either cobalt or iron cyanide anions are loaded on the resin. Cobalt cyanide forms polymeric species in the presence of sulphuric acid, which are extremely difficult to remove from the resin, without the destruction of the resin (Conradie *et al.*, 1995; Fleming and Cromberge, 1984*a*). In the case of iron cyanide, the formation of insoluble double-metal complexes of the form  $M_2Fe(CN)_6$  occur that poison the resin, under the acidic conditions of the elution (Conradie *et al.*, 1995; Fleming and Cromberge, 1984*a*). It is thus recommended that this elution method should not be considered in processes where large amounts of cobalt and iron cyanide complexes are loaded on the resin.

Some of the advantages and disadvantages associated with the elution of aurocyanide with acidic thiourea include (Dicinoski, 1994; Fleming and Cromberge, 1984*a*; Conradie *et al.*, 1995):

**Advantages:**

- No regeneration needed,
- Fast kinetics and compatible with acid washing,
- Non-toxic chemical needed.

**Disadvantages:**

- Poor base metal elution,
- Decomposition of thiourea in acid solution,
- Formation of metal complexes that poison resin.



# Chapter 4

## Materials and Methods

### 4.1 Materials and Analysis

#### 4.1.1 Materials

All the chemicals used in the experiments were of analytical-reagent grade obtained from either Merck or Sigma Aldrich. Synthetic solutions were prepared using  $K_2Pd(CN)_4 \cdot H_2O$  (99%, Sigma-Aldrich),  $K_2Pt(CN)_4 \cdot H_2O$  (98%, Sigma-Aldrich),  $KAu(CN)_2$  (99%, Sigma-Aldrich),  $CuCN$  (99%, Sigma-Aldrich),  $K_2Ni(CN)_4$  (Sigma-Aldrich),  $K_4Fe(CN)_6 \cdot 3H_2O$  (98.5%, Sigma Aldrich) and  $ZnCN_2$  (98%, Merck). The metal salts were mixed with distilled water, in the required quantities needed for each experiment.

In the cases when  $ZnCN_2$  and  $CuCN$  were used, the molar ratios of cyanide to metal salts used were 4 to 1. In the majority of experiments the free cyanide concentration of the stock solutions was adjusted to 150 ppm with use of  $NaCN$ , to keep the metal cyanide complexes in their most stable form, as  $Fe(CN)_4^{6-}$ ,  $Cu(CN)_4^{3-}$ ,  $Cu(CN)_3^{2-}$ ,  $Zn(CN)_4^{2-}$ ,  $Ni(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$ ,  $Pt(CN)_4^{2-}$  and  $Au(CN)_2^-$ .

For the acidic thiourea elution experiments,  $CS(NH_2)_2$  (Merck) was mixed with  $H_2SO_4$  (Sigma Aldrich) along with distilled water. The zinc cyanide eluant was made up by mixing  $ZnCN_2$  with  $NaCN$  in a 1 to 4 molar ratio, in distilled water. The potassium thiocyanate eluant was made up by mixing  $KSCN$  (Sigma Aldrich) with distilled water.

The pH adjustments for all experiments were made by using either  $NaOH$  or  $HCl$ .

#### 4.1.2 Analysis

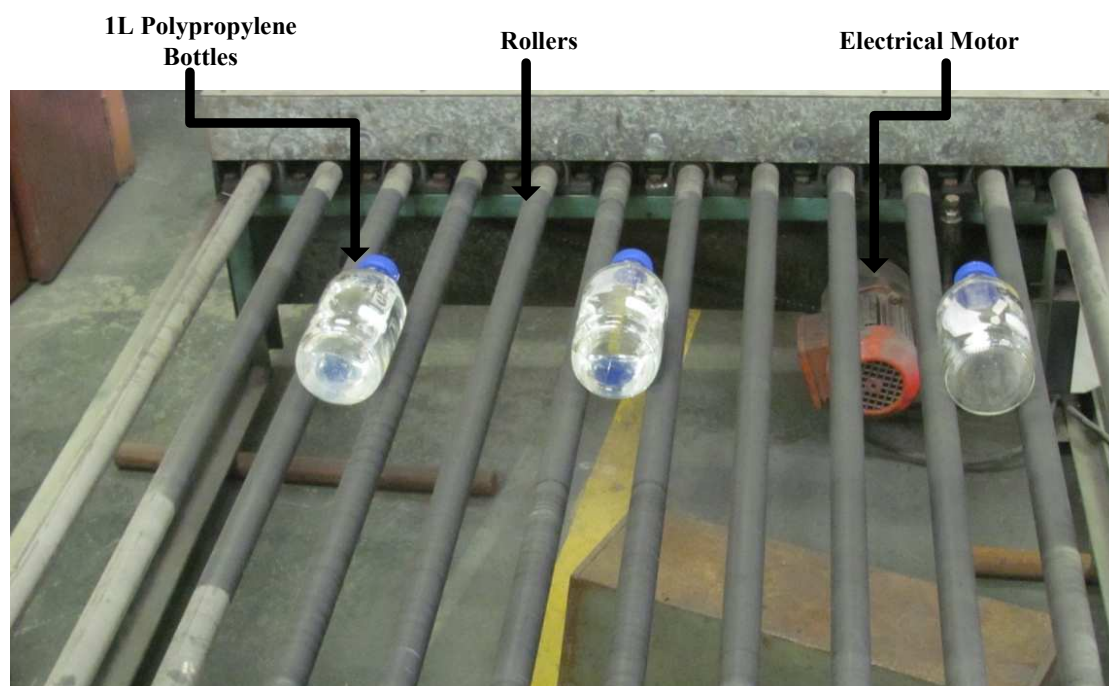
Inductively Coupled Mass Spectroscopy (ICP-MS) or Inductively Coupled Optical Emission Spectroscopy (ICP-OES) was used in all experiments for determination of metal ions in solution. Depending on the concentrations of metals in solution expected, the appro-

priate analysis was selected for low metal concentrations ( $< 1$  ppm), ICP-MS was used, and for high metal concentrations ( $> 1$  ppm), ICP-OES was used.

The free cyanide concentration was determined by potentiometric titration with silver nitrate.

## 4.2 Adsorption Experiments

### 4.2.1 Experimental Setup



**Figure 4.1:** Experimental set-up used for adsorption experiments

Figure 4.1, show the experimental set-up that was used for the majority of the adsorption experiments. It is a very simple set-up that consists only of rollers on which the solution is contacted with the adsorbents. The bottles containing the solution and resin were rolled at 180 rpm at room temperature for the majority of adsorption experiments. The bottles used in all the loading experiments, had a one litre quantity, which were sufficient for the experiments performed.

### 4.2.2 Resin Preparation

Known quantities of resins were transferred to a glass column. Firstly the column was back washed with distilled water. This was done to remove all small and unwanted particles from the resin bed. The resins were then washed with 10 bed volumes of distilled water

over a two-hour period. Six bed volumes of a 1M *NaCl* solution were then passed through the bed over a two-hour period. This was done to ensure that all the active sites on each resin were in the chloride form. After the sodium chloride (*NaCl*) solution was passed through the resin bed, the resin was again washed with 10-bed volumes of water over a 2-hour period. This was done to ensure that all the sodium chloride solution was removed from the resin pores. The resin was then transferred from the column to a closed container where it was stored in distilled water until needed.

### 4.2.3 Screening Different Resins

Twelve ion exchange resins were screened to investigate the adsorption potential of platinum, palladium and gold from the cyanide solution. One millilitre of each resin was transferred into one litre polypropylene bottles that contained one litre of synthetic cyanide solution.

The samples were analyzed for all metals present in the solution, using ICP-MS analysis, after which metal loading was determined by mass balance, as shown in Equation (4.2.1).

$$q_r = \frac{(C_i - C_e)V_s}{V_r} \quad (4.2.1)$$

where,  $q_r$  is the metal loading on the resin in mg/l;  $C_i$  and  $C_e$  are the concentrations of a metal, at the beginning and end of the experiment (mg/l), respectively;  $V_s$  is the volume (l) of solution used; and  $V_r$  is the volume (l) of resin used.

### 4.2.4 Batch Kinetics

Known quantities of the four resins selected from the screening results were transferred to one litre bottles, after which solution was added, to obtain the correct resin-to-solution ratios needed. The bottles were then placed on rollers and rolled for 48 hours at  $\pm 22^\circ\text{C}$ . Samples were collected from each bottle at predetermined time intervals of 1, 2, 3, 4, 8, 16, 24, 36 and 48 hours.

The samples were analyzed for each metal by ICP-MS, after which metal loading was determined by a mass balance. The results were used to generate recovery and loading profiles for each of the four resins.

### 4.2.5 Isotherm Generation

For both the single component and multi-component isotherms generated, seven resin-to-solution ratios of between 1:10000 and 1:800, were used for each of four resins tested. This

generated seven isotherm points for each resin, per experiment performed. The resins for each resin-to-solution ratio were contacted with either one litre single or multicomponent solution for 48 hours in rolling bottles. A sample of each solution was taken before and after each experiment, for ICP-MS analysis, after which the metal loading was determined by mass balance.

For the single component isotherms, synthetic solutions were made up that contained either gold (0.1 ppm), platinum (0.15 ppm) or palladium (0.4 ppm), at a pH of 10.5. No free cyanide was added to these solutions, and thus these metals in their cyanide complexes were the only anions present in the solutions, with the exception of the hydroxide ions.

For the multicomponent isotherms, synthetic solutions were made up that contained gold (0.1 ppm), platinum (0.15 ppm), palladium (0.4 ppm), zinc (5 ppm), nickel (5 ppm), copper (10 ppm) and iron (10 ppm) at a pH of 10.5, and containing a free cyanide concentration of 150 ppm.

#### 4.2.6 Repeated Loading

One millilitre of each resin tested was contacted with one litre synthetic solution, containing gold (0.1 ppm), platinum (0.15 ppm), palladium (0.4 ppm), zinc (5 ppm), nickel (5 ppm), copper (10 ppm) and iron (10 ppm) at a pH of 10.5, with a free cyanide concentration of 150 ppm, for 24 hours in rolling bottles. After 24 hours of contact the resin was filtered from the solution using a vacuum filter. The loaded resin was then re-introduced into a fresh synthetic solution, with the same composition as previously described, for another 24 hours on rolling bottles. The procedure was repeated nine times for each of the four resins investigated.

Before and after each contact a sample was taken from the solution for ICP-MS analysis. The cumulative loading on each resin over the nine contacts was then calculated by a mass balance over each contact.

#### 4.2.7 Effect of pH

Synthetic solutions containing gold (0.1 ppm), platinum (0.15 ppm), palladium (0.4 ppm), zinc (5 ppm), nickel (5 ppm), copper (10 ppm) and iron (10 ppm), at four different pH's of 9, 10, 11 and 12 were prepared. One millilitre of each resin was contacted with 1L of solution for 48 hours in rolling bottles.

A sample of the solution was taken before and after each contact, for ICP-MS analysis. Metal loading was then determined by a mass balance, after which the loading of each metal in solution could be plotted against the different solution pH's.

### 4.2.8 Effect of Base Metal Concentration

From the adsorption results discussed throughout the report, it was observed that zinc cyanide and nickel cyanide achieved the highest loading onto both Minix and Amberlite PWA-5, and thus it was concluded that these two base metal cyanides will affect the loading of gold, platinum and palladium the most.

Solutions were prepared that contained gold (0.1 ppm), platinum (0.15 ppm) and palladium (0.4 ppm) with 150 ppm free cyanide concentration at pH 10.5. Zinc cyanide and nickel cyanide were added to each solution, so as to ultimately have three solutions containing 5 ppm, 10 ppm and 20 ppm of nickel and zinc, respectively. One millilitre wet settled resin, of either Minix or Amberlite PWA-5, was added to each solution in one litre bottles and placed on rollers for 48 hours.

Samples were taken at 30, 60, 90, 120, 180, 240 and 2880 minutes during the experiment. The majority of samples that were taken up to 240 minutes were used to calculate an initial loading rate for each of the metals present in the solution. The sample taken at 2880 minutes was used to calculate the equilibrium loading of each metal in the solution.

### 4.2.9 Effect of Precious Metal Concentration

Solutions were prepared that contained zinc (5 ppm), nickel (5 ppm), copper (10 ppm) and iron (10 ppm) with a free cyanide concentration of 150 ppm and pH 10.5. Gold, platinum and palladium concentrations were varied within each solution, between 0.1 ppm and 0.3 ppm for gold, between 0.15 ppm and 0.45 ppm for platinum and between 0.4 ppm and 1.2 ppm for palladium. One millilitre of wet settled resin, of either Minix or Amberlite PWA-5, was added to each one litre synthetic solution, and then placed on rollers for 48 hours.

Samples were taken at 30, 60, 90, 120, 180, 240 and 2880 minutes during the experiment. The majority of the samples that were taken up to 240 minutes were used to calculate an initial loading rate for each of the metals present in the solution. The sample taken at 2880 minutes was used to calculate the equilibrium loading of each metal in the solution.

### 4.2.10 Effect of Temperature

Solutions containing gold (5 ppm), platinum (5 ppm) and palladium (5 ppm) with a free cyanide concentration of 150 ppm at pH 10.5 were prepared. One millilitre wet-settled resin, of either Minix or Amberlite PWA-5, was added to one litre of the solution.

The one litre solutions were then transferred to one litre beakers, in water baths with overhead stirrers. The water baths were at different temperatures of 30°C, 40°C,

50°C and 60°C, respectively. Each beaker had a cover to minimize evaporation from the beakers. Each experiment was performed for 48 hours, with the solutions being stirred at approximately 180 rpm.

Samples were taken from each solution, at 30, 60, 90, 120, 180, 240, 300, 360, 420, 480 and 2880 minutes during the experiment. The majority of samples that were taken up to 480 minutes were used to calculate an initial loading rate for each of the metals present in the solution. The sample taken at 2880 minutes was used to calculate the equilibrium loading of each metal in the solution.

## 4.3 Elution Experiments

### 4.3.1 Experimental Setup

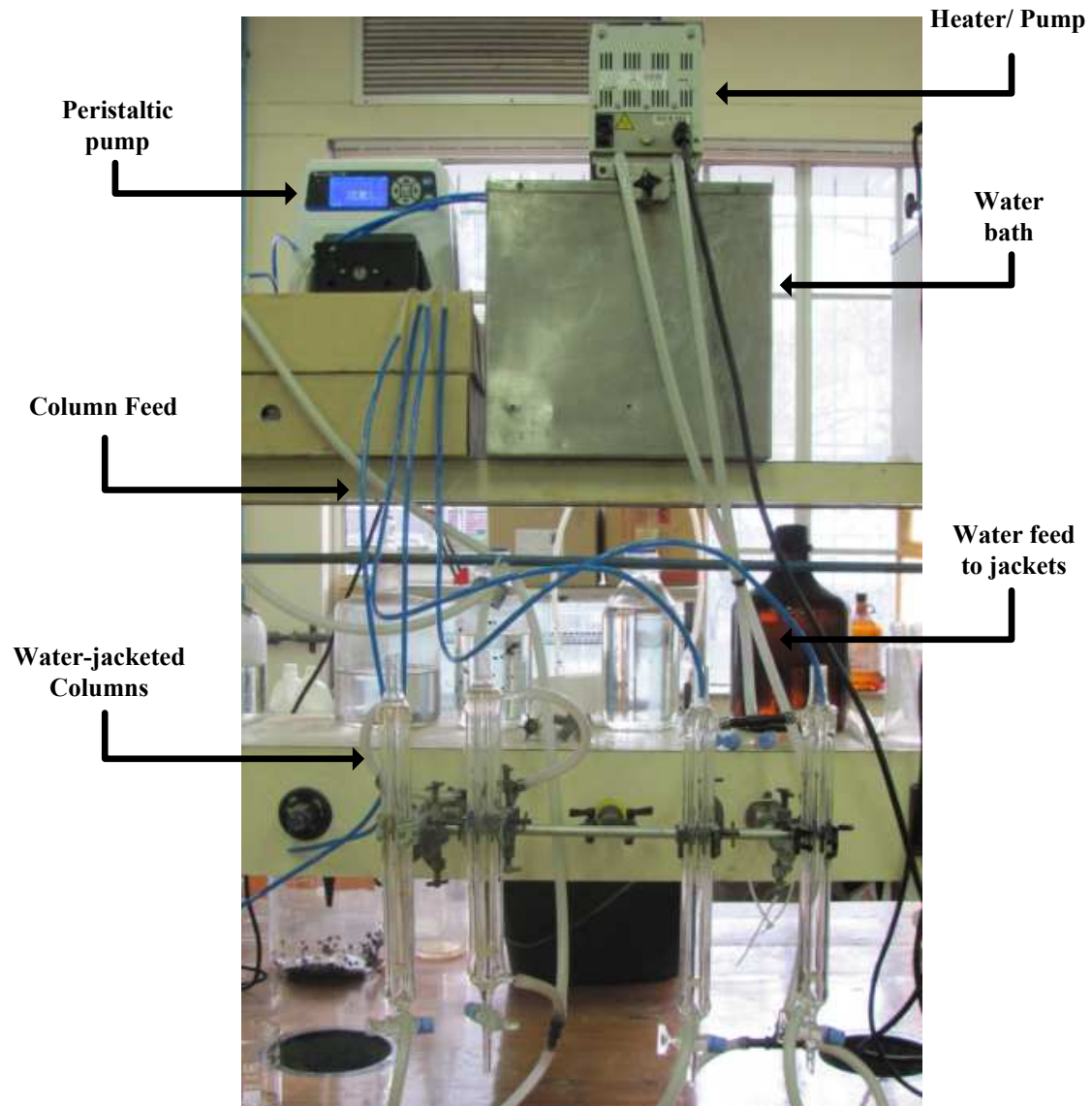


Figure 4.2: Experimental setup for the elution experiments

Figure 4.2 shows the experimental setup that was used for all the elution experiments. This primarily consists of water baths, a peristaltic pump and water-jacketed glass columns.

### 4.3.2 Loading of Resins for Elution

For the majority of elution experiments, solutions that contained 15 ppm of gold, 15 ppm of platinum and 15 ppm of palladium with a free cyanide concentration of 150 ppm and

pH 10.5, were used to load the resins. Five millilitres of resin were added to one litre of solution, and placed on rollers for 48 hours. Samples were taken before and after each loading and the loading on the resin was determined by mass balance. The results of the analysis indicated that 5 ml resin consistently achieved the same loading during each loading.

For the elution of both precious and base metals, five millilitre of resin were loaded with a solution containing gold (10 ppm), platinum (10 ppm), palladium (10 ppm), zinc (10 ppm), nickel (10 ppm), copper (10 ppm) and iron (10 ppm) with a free cyanide concentration of 150 ppm at pH 10.5, on rollers for 48 hours.

### 4.3.3 Screening Eluting Agents

The three eluting agents that were being investigated for the elution of aurocyanide from anion exchange resins were tested, namely acidic thiourea, zinc cyanide and potassium thiocyanate. Five millilitres of loaded resin was transferred into glass columns as shown in Figure 4.3.1. Each eluting agent was placed in the water baths above the columns and the temperature of the water baths were set to 22°C for potassium thiocyanate, 50°C for zinc cyanide and 60°C for acidic thiourea.

Each elution was performed at a flow rate of 10 BV/h, with samples taken of each bed volume of eluate flowing through the column. Each experiment was stopped after 25 bed volumes of eluate had passed through the column. The samples were then analyzed with ICP-OES, after which the results were used to generate eluate concentration and elution profiles for each elution method.

### 4.3.4 Effect of Concentration

During this experiment, the concentration of each eluting agent was changed for each experiment performed. For acidic thiourea the thiourea concentration was varied between 0.1 M and 0.5 M in increments of 0.1 M, while the hydrochloric acid concentration was varied between 0.1 M and 0.5 M also in increments of 0.1 M. For zinc cyanide, the zinc cyanide concentrations tested were 0.15 M, 0.3 M, 0.5 M and 0.7 M. For potassium thiocyanate the concentrations tested were 0.5 M, 1 M, 1.5 M and 2 M.

For each experiment only the concentration of each eluting agent was varied while the other conditions remained constant. Again, five millilitres of loaded resin was transferred into a glass column for each experiment. During this experiment all the eluate flowing through the column was collected in a beaker at the bottom of each column, and a sample was taken from the solution in the beaker after 15 bed volumes of eluate had passed through the column, and taken for ICP-OES analysis.



### 4.3.5 Effect of Flow Rate

During this experiment the concentration of each eluting agent and the temperature at which each elution was performed were held constant, while the flow rate was varied. The elution flow rates investigated were 5 BV/h, 10 BV/h, 15 BV/h and 20 BV/h.

Five millilitres of loaded resin was transferred into a glass column for each experiment. During this experiment all the eluate flowing through the column was collected in a beaker at the bottom of each column, and a sample was taken from the solution in the beaker after 15 bed volumes of eluate had passed through the column, and taken for ICP-OES analysis.

### 4.3.6 Effect of Temperature

During this experiment the concentration of each eluting agent and the elution flow rate were held constant, while the temperature was varied. For acidic thiourea and zinc cyanide the temperature was varied between 30°C and 60°C, in increments of 10°C. For potassium thiocyanate the temperatures at which investigation took place were 22°C, 30°C, 40°C and 50°C.

Five millilitres of loaded resin was transferred into a glass column for each experiment. During this experiment all the eluate flowing through the column was collected in a beaker at the bottom of each column, and a sample was taken from the solution in the beaker after 15 bed volumes of eluate had passed through the column, and taken for ICP-OES analysis.

### 4.3.7 Base Metal Elution Efficiency

Five millilitres of loaded resin, loaded as described in Section 4.3.2, was transferred into glass columns. Eluting agents were placed in the water baths above the columns, to achieve the optimal conditions for each elution. The loaded resins were eluted at a flow rate of 10 BV/h and samples of each bed volume of eluate were taken. The experiment was stopped after 20 bed volumes had passed through the column. The samples were then analyzed with ICP-OES, after which the results were used to generate eluate concentration and elution profiles for each elution method.

## Chapter 5

# Adsorption: Results and Discussion

### 5.1 Screening Test

Before any experiments were performed, two blank experiments were done, to confirm that the adsorption observed during subsequent experimentation was strictly a result of anion exchange and not caused by the complexes adhering to the walls of the polypropylene bottles. The experiments consisted of contacting one litre of the stock solution in Table 5.1, with the polypropylene bottles, without any anion exchange resin present, for 24 hours.

**Table 5.1:** Synthetic cyanide solution (Free cyanide concentration, 150ppm; pH 10.5)

Metal	Concentration (ppm)
Au	0.1
Pt	0.15
Pd	0.4
Cu	10
Ni	5
Fe	10
Zn	5

Both of the blank tests indicated that none of the metals were extracted from the solutions onto the walls of the polypropylene bottles. It was then concluded that any decrease in metal concentration during subsequent experimentation will be a result of anion exchange taking place between the metal cyano complexes and resins investigated. Twelve resins consisting of strong base (SB), weak base (WB) and chelating resins were screened to observe the recovery potential of platinum, palladium and gold from the cyanide solution. The resin selection was based on manufacturer recommendations and literature, and are shown in Table 5.2.

**Table 5.2:** Properties of ion exchange resins screened

Resin	Type	Matrix	Functional Group	Capacity (eq/l)
Dowex 21K XLT	SB	STY-DVB	Trimethyl	1.4
Ambersep 900	SB	STY-DVB	Trimethyl	1.0
Amberlite IRA 478RF	SB	Acrylic	Trimethyl	1.25
Purolite A500	SB	STY-DVB	Trimethyl	1.15
Puopack PPA 400	SB	STY-DVB	Trimethyl	1.3
Amberjet 4600	SB	STY-DVB	Dimethyl Ethanol	1.25
Amberlite PWA-5	SB	STY-DVB	Tri-ethyl	1.0
Ambersep 920U	SB	MR	Tri-ethyl	1.0
XZ - 91419 (Minix)	SB	STY-DVB	Tri-butyl	0.3
XUS 43600	Chelating	STY-DVB	Thiouonium	0.7
S 920	Chelating	STY-DVB	Isothiouonium	
S 985	WB	Acrylic	Polyamine	2.3

The screening tests were designed in such a way that an excess of active sites was available, in relation to the anions present in the solution. The first screening experiment was performed using a resin-to-solution ratio of 1:500. However, from the results of this screening experiment, selectivity for only a few resins could be seen, because of the excessive amount of active sites. A subsequent screening experiment was then performed, in which the anion exchange capacity was reduced, by using a resin-to-solution ratio of 1:2000, from which selectivity could be observed. The screening results for all 12 resins are shown in Table 5.3.

From Table 5.3 it can be observed that the five strong base resins containing trimethyl functionality, Dowex 21K XLT, Ambersep 900, Purolite A500 and Puopack PPA, with the exception of Amberlite IRA 48RF, had similar recoveries of platinum, palladium and gold from the cyanide solution. This result was expected, based on the discussion on functionality in Section 3.6.4. The base metal recoveries of these resins were very similar, with the loading of iron and copper being lower than that for nickel and zinc. Amberjet 4600, containing a dimethyl ethanol functionality, showed similar recovery results than those of the strong base resins that contained trimethyl functionality, with high recoveries of platinum and palladium and moderate recoveries of gold, zinc, nickel, copper and iron from the cyanide solution.

The recoveries obtained for Amberlite PWA-5 and Ambersep 920U, both containing tri-ethyl functionalities, were different for all metals. Amberlite PWA-5 was more selective for the divalent cyanide complexes of platinum, palladium, zinc and nickel and the monovalent aurocyanide complex, with poor recoveries of iron and copper from the cyanide solution. Ambersep 920U on the other hand, was selective for the divalent cyanide

Table 5.3: Screening results

Metal		Metal Concentration(mg/l)						
		Fe	Ni	Cu	Zn	Pd	Pt	Au
Stock Solution [CN <sup>-</sup> ] = 150 mg/l		10	5	10	5	0.4	0.15	0.1
Resin	Resin to Solution	% Metal Adsorbed						
Dowex 21K XLT	1 to 2000	43	78	40	80	89	92	62
Ambersep 900	1 to 2000	44	70	44	55	84	88	51
Amberlite IRA 48RF	1 to 2000	35	16	14	12	28	37	5
Purolite A 500	1 to 2000	46	67	40	60	82	84	69
Puropack PPA 400	1 to 2000	49	76	45	71	90	92	58
Amberjet 4600	1 to 2000	56	71	29	62	84	87	56
Amberlite PWA-5	1 to 2000	3	88	48	94	95	96	76
Ambersep 920U	1 to 2000	35	46	27	48	57	65	35
XZ-91419 (Minix)	1 to 500	0	45	16	70	71	77	98
XUS 43600	1 to 500	0	9	0	12	20	19	61
S 920	1 to 2000	14	24	11	24	36	41	71
S 985	1 to 2000	50	40	32	47	55	65	7

complexes of platinum, palladium, zinc and nickel, but their recoveries were lower than for Amberlite PWA-5. A possible reason for this could be the difference in the matrices of the two resins. Amberlite PWA-5 consists of a STY-DVB matrix, that is much more compatible with lower charged, or less hydrated anions, whereas Ambersep 920U consists of a macrorecticular matrix, that is more compatible with highly charged anions or more hydrated anions, such as the cyanide complexes of iron and copper. Thus it can be expected that more iron and copper will load onto Ambersep 920U, decreasing the loading of other metals on the resin.

Minix selectively recovered all the gold from the cyanide solution. This was consistent with literature, in which the selectivity of Minix for the monovalent  $Au(CN)_2^-$  anion was discussed (Kotze *et al.*, 2005; Van Deventer *et al.*, 1999). Good recoveries of platinum, palladium and zinc were also obtained with Minix, with moderate recovery of nickel and poor recovery of copper and iron from the cyanide solution.

XUS 43600 showed poor recoveries of all metals, with the exception of gold. It was concluded that the thiuronium group on this resin was hydrolyzed under the high pH conditions of the solution, which decreased the resin's exchange capacity. The other two resins, S 920 and S 985, a chelating and weak base resin respectively, also showed poor recoveries of all metals from solution, with no clear indication of a higher affinity for a group or certain metal cyanide. It was concluded that the high pH of the solution decreased the exchange capacities of these resins by converting most of their protonated sites to the free base form, which resulted in poor recoveries of all metal anions.

From the screening results it can be concluded that the resins with the highest plat-

inum, palladium and gold recovery potential from the cyanide solution, along with moderate base metal recovery were, Dowex 21K XLT, Ambersep 900, Purolite A500, Puropack PPA 400, Amberjet 4600, Amberlite PWA-5 and Minix. As discussed in Section 3.6.4, strong base anion exchange resins that contain trimethyl functional groups will in most cases, show non-selective adsorption. From the screening results, high platinum and palladium recoveries ( $> 85\%$ ) were observed for these resins with moderate recovery of gold ( $< 69\%$ ) from the cyanide solution. The low recovery of gold compared with that of platinum and palladium for these resins, could be attributed to the high ionic density of these resins, which will result in their having a higher affinity for higher charged anions, such as  $Pt(CN)_4^{2-}$  and  $Pd(CN)_4^{2-}$ , than for a lower charge anion such as  $Au(CN)_2^-$ . Although the base metal recoveries for these resins were relatively high (between 43% and 80%), when their respective concentrations in the feed solution are considered, the fact that they showed high recoveries of platinum and palladium, make them worth further investigation. Similar results, as mentioned earlier, were seen for Amberjet 4600, which contains a dimethyl ethanol functionality.

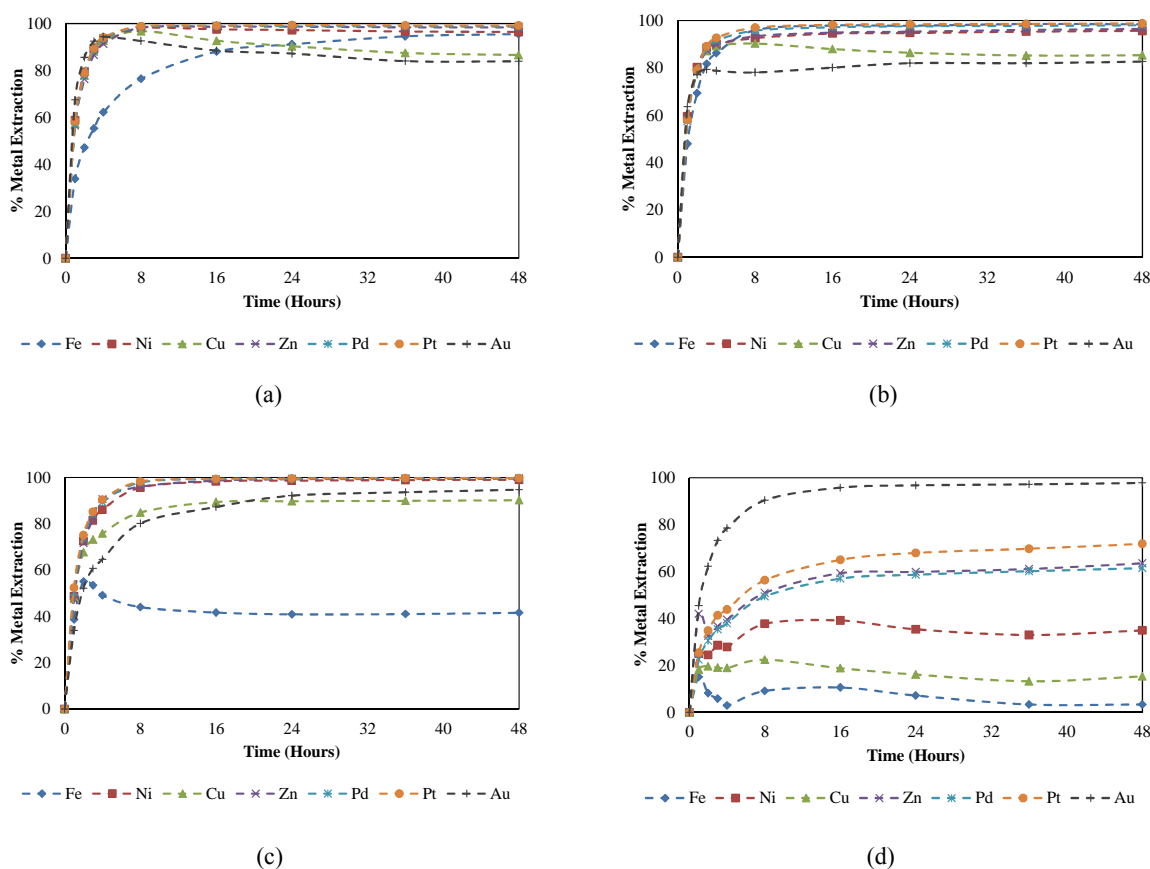
Amberlite PWA-5 had a high affinity for the divalent anions of,  $Pt(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$ ,  $Ni(CN)_4^{2-}$  and  $Zn(CN)_4^{2-}$ , over all other metal cyanide anions in solution. This observation is consistent with studies (Riveros, 1993; Versiane and Ciminelli, 2000), in which the anion exchange resin, HP 555's containing a tri-ethyl functionality, was found to have a high affinity for the lower charged cyanide anions of nickel and zinc. This was the reason that Amberlite PWA-5, which is the industrial version of HP 555's that was used in the study by Riveros, (1993), was included in this study because it was hypothesized that the resin will also have an high affinity towards the divalent metal cyanide anions of platinum and palladium. The recovery of gold by Amberlite PWA-5 was high compared to that of the strong base resins that contained trimethyl functionality. The recovery of copper and iron was poor, which could be a result of the larger functional group of Amberlite PWA-5, which imposed a sterical effect that hindered the loading of the highly charged anions,  $Fe(CN)_6^{4-}$  and  $Cu(CN)_4^{3-}$ .

The low exchange capacity of Minix, along with its large tri-butyl functionality, made the resin very selective for the monovalent  $Au(CN)_2^-$  anion. Moderate recoveries of platinum, palladium and zinc were also observed for Minix, with poor recovery of copper and iron from the cyanide solution. This indicated that the resin had a high affinity for low charged anions, and a poor extract ability of higher charged anions. Again this can be explained by the large functional group on Minix that hindered the adsorption of  $Fe(CN)_6^{4-}$  and  $Cu(CN)_4^{3-}$ , and also the low exchange capacity of the resin, which will result in the active sites spreading far from each other on the resin, making the adsorption of these metal cyanide anions difficult.

After the screening, four of the resins, Dowex 21K XLT, Amberjet 4600, Amberlite PWA-5 and Minix were selected for subsequent experimentation. The product data sheets for the four resins are presented in Appendix B. The selection was made on the basis of platinum, palladium and gold recovery potentials, low base metal recovery, and having resins that contain different functionalities and exchange capacities, so that these features could be investigated and compared further.

## 5.2 Batch Kinetics

Batch kinetic experiments were performed to evaluate the time needed to reach equilibrium between the solution and adsorbents, and also to observe the adsorption path of each metal over time onto the four anion exchange resins. The experiment was performed using a resin-to-solution ratio of 1:1000, this ratio was selected to create a competitive environment between the different metal cyanide anions in solution. The extraction profiles for each resin over a 48 hour period, are shown in Figure 5.1. From Figure 5.1, it can



**Figure 5.1:** Batch kinetic extraction profiles for (a) Dowex 21K XLT, (b) Amberjet 4600, (c) Amberlite PWA-5 and (d) Minix

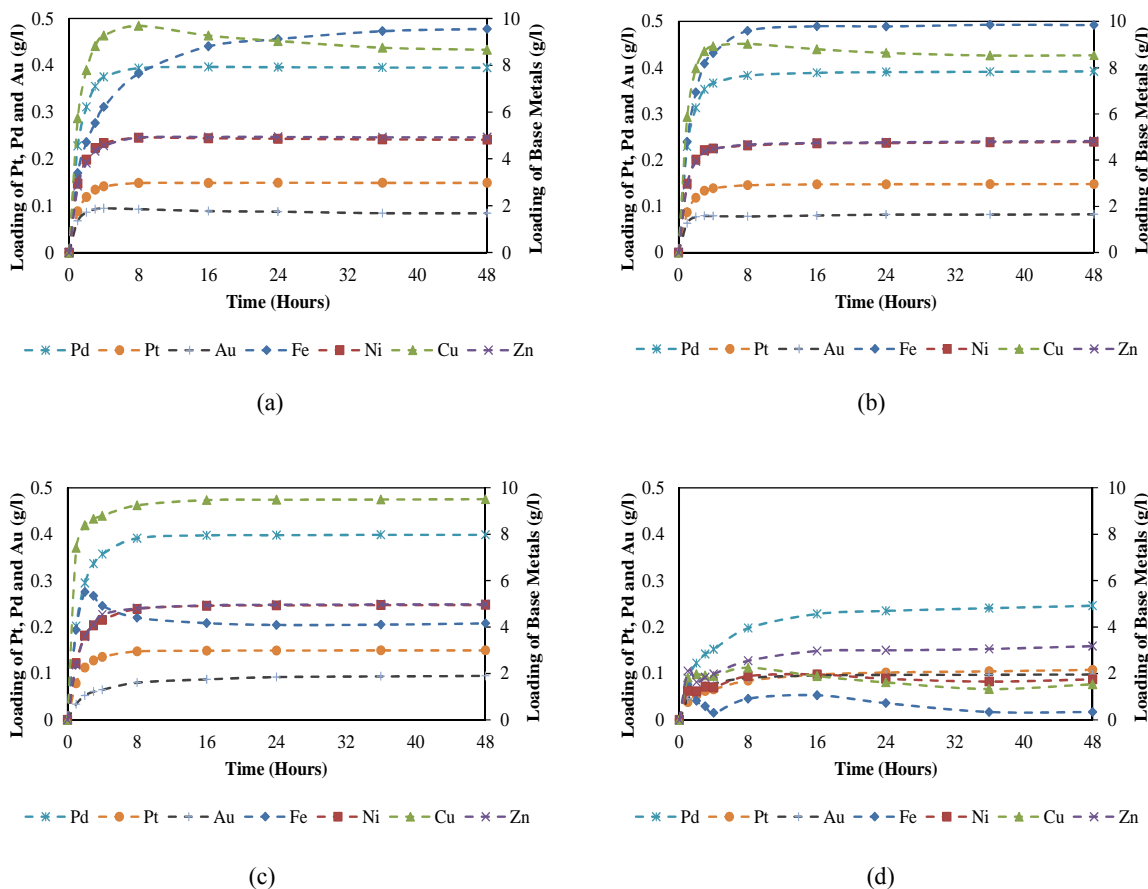
be seen that 48 hours were sufficient for all four resins to reach equilibrium. From Figure

5.1(a) and Figure 5.1(b) it can be seen that the extraction profiles for Dowex 21K XLT and Amberjet 4600 were similar, as mentioned in Section 5.1. All metals, except gold and copper, could be completely recovered from the cyanide solution. The reason for the lower recovery of gold and copper can be explained by the charge of the copper and gold cyanide anions. The high ionic density of these two resins gives them a higher affinity for the more highly charged anions in the solution. Since gold is present as the monovalent  $Au(CN)_2^-$  anion and a fraction of the copper will be present in its monovalent state as,  $Cu(CN)_2^-$ , these two anions will have poorer recoveries than the other metal cyanide anions in solution.

The difference in the recovery of metals, when using resins with lower ionic densities and larger functional groups can be seen when comparing Figures 5.1 (a) and (b), with Figures 5.1 (c) and (d). Complete recovery of all metals, except for iron, copper and gold was achieved with the use of Amberlite PWA-5. This confirms the high affinity that this resin exhibits for the divalent metal cyanide anions of platinum, palladium, nickel and zinc. Gold recovery reached 95% at equilibrium, followed by copper with a recovery of 90%. Iron was poorly recovered with the use of Amberlite PWA-5, with a recovery of 42%. The poor iron recovery can be explained by considering the larger functional group and lower ionic density of Amberlite PWA-5. The adsorption of the large tetravalent  $Fe(CN)_6^{4-}$  anion will be sterically hindered by the larger tri-ethyl functional group of Amberlite PWA-5, and the lower ionic density will cause the active sites on the resin matrix to be spaced further away from each other, making the adsorption of  $Fe(CN)_6^{4-}$  difficult. Thus for Amberlite PWA-5, iron cyanide is initially adsorbed by the resin, but as the resin becomes loaded the iron cyanide is being displaced by the divalent metal-cyanide complexes, for which Amberlite PWA-5 has a higher affinity.

Minix, as was seen in Section 5.1, was very selective for gold. Gold was the only metal present in the solution that reached a recovery of almost 100%. It is also evident from Figure 5.1(d) that in the case of Minix the recoveries of all metals except for gold were much lower compared with the other three resins. This is due to the much lower exchange capacity of Minix, compared with the other resins, which is one of the characteristics of Minix that makes it so selective for the monovalent  $Au(CN)_2^-$  anion. Gold recovery was followed by 72%, 64% and 61% recovery of platinum, zinc and palladium, respectively, with the lowest recoveries reached for nickel, copper and iron, of 35%, 15% and 5%, respectively. Thus the large tri-butyl functional group along with the low exchange capacity of Minix makes this resin very selective for monovalent anions, followed by divalent anions, with a very low affinity for tri- and tetra-valent anions.

To put the extraction profiles in Figure 5.1 into perspective, loading profiles for each of the resins were generated along with the recoveries and loading of each metal on the



**Figure 5.2:** Batch kinetic loading profiles for (a) Dowex 21K XLT, (b) Amberjet 4600, (c) Amberlite PWA-5 and (d) Minix

respective resins at equilibrium, which is shown in Figure 5.2 and Table 5.4. The loading of base and precious metals was plotted on two separate axes, because the loading of platinum, palladium and gold was an order of magnitude lower than the loading of the base metals. If the extraction profiles in Figure 5.1 and the loading profiles in Figure 5.2 are compared, a difference is immediately noticed. Although the recoveries of platinum, palladium and gold are in most cases higher than 90%, their loading on the resins is in some cases up to 25 times lower than that of the base metals that were poorly recovered. For example, when comparing the recoveries and loadings of metals after 48 hours onto Minix in Table 5.4, it is clear that although only 3% of iron was recovered, the loading of iron was still three times higher than the loading of gold that reached a recovery of 98%.

Thus from the batch kinetic results, it is clear that the recovery of metals from solution provides insufficient information on what is actually happening during the adsorption. Although the recoveries of platinum, palladium and gold are high and those of the base metals are low, platinum, palladium and gold still make up only a small fraction of the total metal loading on the respective resins. The reason for this is the low concentration of platinum, palladium and gold in solution compared to the high concentration of base



**Table 5.4:** % Extraction and loading of metals after 48 hours of contact with the respective anion exchange resins

Resin	% Metal Extraction						
	Fe	Ni	Cu	Zn	Pd	Pt	Au
Dowex 21K XLT	96	96	87	98	99	99	84
Amberjet 4600	98	96	85	96	98	99	83
Amberlite PWA-5	42	99	90	100	100	100	95
Minix	3	35	15	64	61	72	98
Resin	Metal Loading (g/l)						
	Fe	Ni	Cu	Zn	Pd	Pt	Au
Dowex 21K XLT	9.56	4.82	8.66	4.92	0.39	0.15	0.08
Amberjet 4600	9.85	4.79	8.54	4.82	0.39	0.15	0.08
Amberlite PWA-5	4.16	4.95	9.51	4.98	0.40	0.15	0.09
Minix	0.34	1.75	1.54	3.18	0.25	0.11	0.10

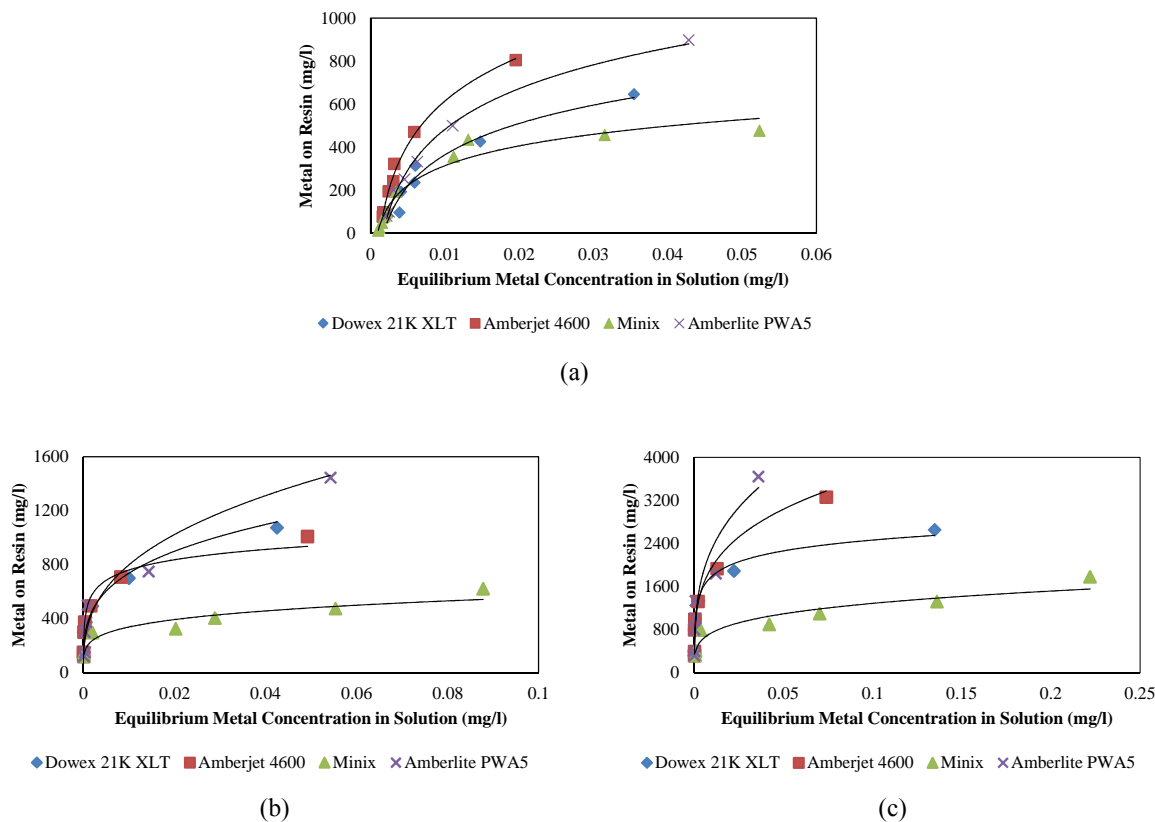
metals in solution. Thus, even if the base metals such as iron and copper are poorly recovered by some of the resins, their concentration in the feed solution makes it possible for them to load much more than the platinum, palladium and gold. The effect of metal concentration in the feed solution will thus have a major impact on the fractional loading of each metal on the resin, whatever the recovery of the metals may be.

## 5.3 Isotherm Studies

### 5.3.1 Single Component Isotherms

Isotherms were generated for gold, platinum and palladium, for the four strong base anionic resins investigated. This was done by contacting one litre of solution, containing either platinum (0.15 ppm), palladium (0.4 ppm) or gold (0.1 ppm), with different volumes of wet-settled resin, for 48 hours in rolling bottles. Each resin-to-solution ratio could then be used to calculate one isotherm point for each metal isotherm. The loading of each metal was determined by the difference of the metal concentration before and after equilibrium. This method of metal loading calculation is susceptible to errors, especially when differences in solution concentration are not large, as this will result in a scatter of isotherm points. This however was not the case during this experiment, with clear isotherm trends generated. Trend lines were fitted to the isotherm data for each resin, to indicate the general trend of the data.

Figure 5.3 represents the isotherms of (a) gold, (b) platinum and (c) palladium, on the four respective strong base anionic resins. From Figure 5.3 (a) it can be seen that the maximum gold loading achieved on the four respective resins was in the range of 550 to 1000 mg/l. This is equivalent to a upgrading ratio of between 5500 to 10000, from a



**Figure 5.3:** Single component isotherms for (a) gold, (b) platinum and (c) palladium, for the 4 respective resins

single component solution containing 0.1 ppm gold. Maximum gold loading on the four respective resins, in decreasing order, was found to be as follows Amberlite PWA-5 > Amberjet 4600 > Dowex 21 K XLT > Minix. The low loading of gold onto the high exchange capacity resin Dowex 21K XLT (1.4 eq/l), can be explained by the fact that this high ionic strength resin had a lower affinity for the lower charged aurocyanide anion. With the exception of Dowex 21K XLT, the loading of gold on the other three anion exchange was as expected, when observing their exchange capacities in Table 5.2.

From Figure 5.3 (b) it can be seen that the maximum platinum loading achieved was between 600 and 1450 mg/l, which is equivalent to an upgrading ratio of between 4000 and 10000, from a single component solution containing 0.15 ppm platinum. The maximum platinum loading achieved on the four resins, in decreasing order, was found to be as follows Amberlite PWA-5 > Dowex 21K XLT > Amberjet 4600 > Minix.

From Figure 5.3 (c) it can be seen that the maximum palladium loading achieved was between 1800 and 3700 mg/l, which is equivalent to an upgrading ratio of between 4500 and 9250, from a single component solution containing 0.4 ppm palladium. The maximum palladium loading achieved on the four resins in decreasing order, was found to be as follows, Amberlite PWA-5 > Amberjet 4600 > Dowex 21K XLT > Minix.

From the isotherm results in Figure 5.3, the highest maximum loading of all three metals were achieved onto Amberlite PWA-5 with lowest maximum loading onto Minix from single component solutions. This was expected due to the much lower exchange capacity of Minix (0.3 eq/l) compared to the other three strong base anionic resins investigated. Relatively high upgrading ratio ranges were also achieved for all 3 metals, when considering the low strength feed solutions used during the isotherm generations.

The Langmuir and Freundlich isotherm models were fitted to the equilibrium data, by linearizing the models as shown in Equations (5.3.1) and (5.3.2), for the Langmuir and Freundlich models respectively.

$$\frac{1}{Q_e} = \left(\frac{1}{BQ_m}\right)\frac{1}{C_e} + \frac{1}{C_m} \quad (5.3.1)$$

$$\text{Log}(Q_e) = \text{Log}(A) + n\text{Log}(C_e) \quad (5.3.2)$$

The corresponding constants for each model were estimated by plotting  $1/Q_e$  against  $1/C_e$  for the Langmuir isotherm, and  $\text{Log } Q_e$  against  $\text{Log } C_e$  for the Freundlich isotherm. Linear trend lines were then fitted to the data in Excel to obtain the constants for each model. The model parameters generated for each metal onto each resin are shown in Tables 5.5, 5.6, and 5.7.

**Table 5.5:** Freundlich and Langmuir model data for gold

Langmuir	Dowex 21K XLT	Amberjet 4600	Amberlite PWA-5	Minix
Qm (mg/l)	905.14	2073.83	1188.35	781.98
B	14.84	21.98	16.04	14.00
$R^2$	0.93	0.93	0.99	0.95
Freundlich	Dowex 21K XLT	Amberjet 4600	Amberlite PWA-5	Minix
A	3.96	3.79	11.02	2.30
n	0.53	0.77	0.64	0.47
$R^2$	0.94	0.98	0.93	0.83

**Table 5.6:** Freundlich and Langmuir model data for platinum

Langmuir	Dowex 21K XLT	Amberjet 4600	Amberlite PWA-5	Minix
Qm (mg/l)	688.85	781.62	637.02	414.16
B	0.34	0.31	0.45	0.37
$R^2$	0.97	0.93	0.78	0.96
Freundlich	Dowex 21K XLT	Amberjet 4600	Amberlite PWA-5	Minix
A	3.23	2.46	4.16	1.08
n	0.32	0.26	0.36	0.22
$R^2$	0.94	0.90	0.87	0.97

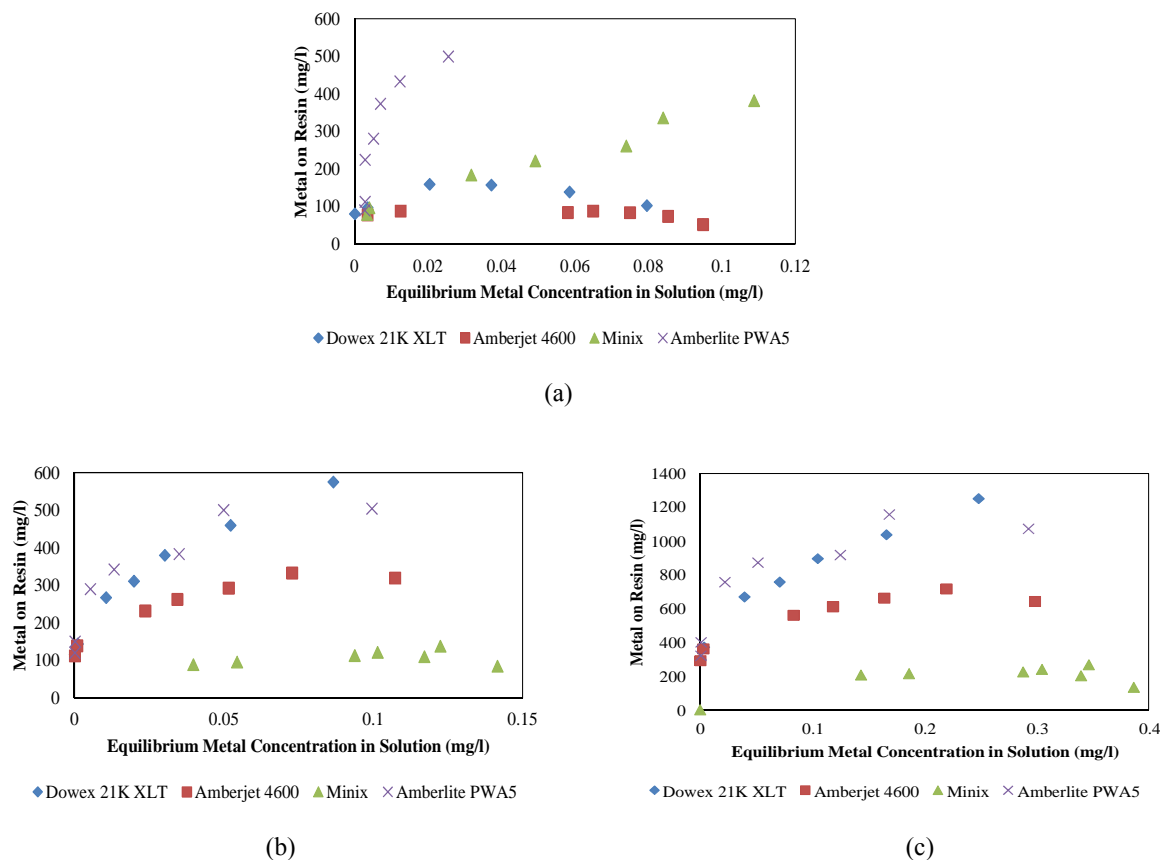
**Table 5.7:** Freundlich and Langmuir model data for palladium

Langmuir	Dowex 21K XLT	Amberjet 4600	Amberlite PWA-5	Minix
Qm (mg/l)	1823.49	1948.56	1854.60	1184.27
B	0.36	0.19	0.19	1.30
$R^2$	0.98	0.96	0.97	0.97
Freundlich	Dowex 21K XLT	Amberjet 4600	Amberlite PWA-5	Minix
A	5.19	6.78	9.56	2.22
n	0.25	0.27	0.31	0.24
$R^2$	0.89	0.89	0.92	0.93

### 5.3.2 Multicomponent Isotherms

The problem with investigating single component solutions is that in actual operations these solutions will contain platinum, palladium, gold and base metals. In actual processes, anion exchange effectiveness will be affected by factors such as the effect of the different anions on each other and also the effect of their respective concentrations in solution, which is not the case in single component systems. Thus although single component solutions can be modelled well to a degree, they merely provide data that can be used to compare them with multicomponent systems.

In this section there is a description of what happens when isotherms were generated from multicomponent solutions containing gold, platinum and palladium along with the base metals zinc, nickel, copper and iron, all present in their cyanide complexes. The process followed was the same as with the single component isotherm generations. The concentrations of all metals in solution were the same as presented in Table 5.1. Trend lines were again fitted to the isotherms of gold, platinum and palladium, in order to compare them with their single component isotherms, this was however not performed for the base metal isotherms. No attempt was made to fit equilibrium models to the data, because the Langmuir and Freundlich equilibrium models were specifically developed for single component systems.



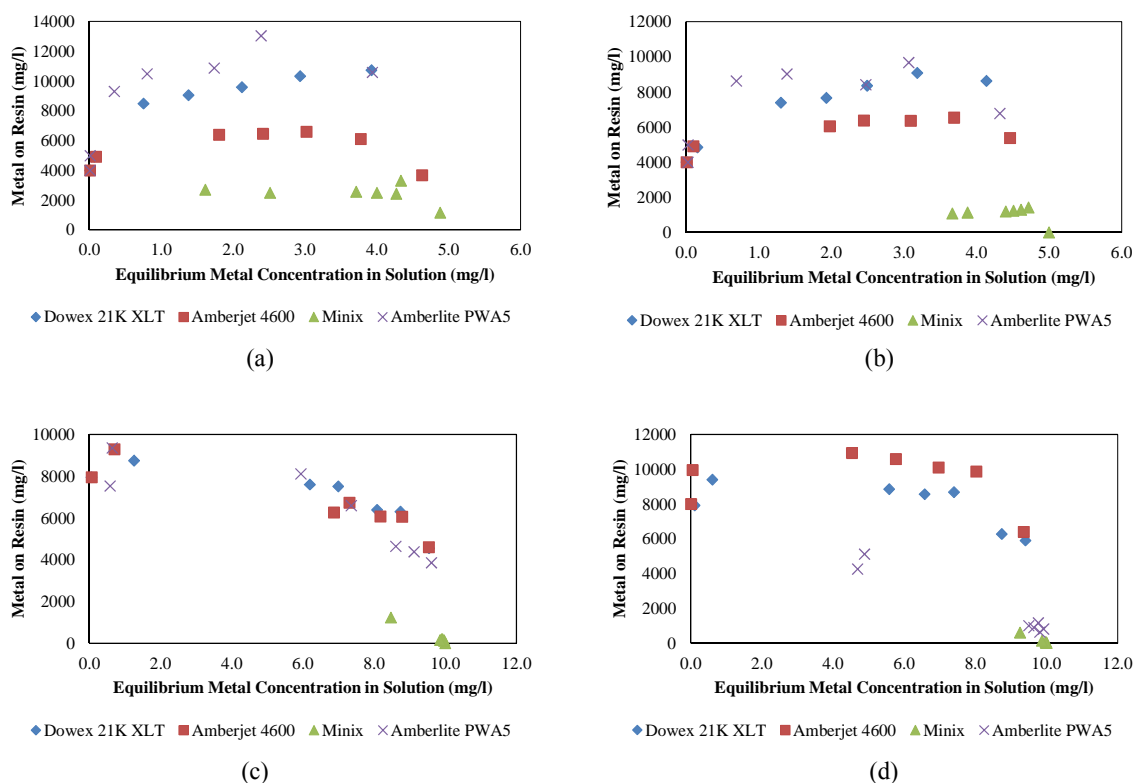
**Figure 5.4:** Isotherms for (a) gold, (b) platinum and (c) palladium, for the 4 respective resins, generated from a multicomponent solution

Figure 5.4 represents the multicomponent isotherms for (a) gold, (b) platinum and (c) palladium. From Figure 5.4 (a) it can be seen that the maximum gold loading achieved from a multicomponent solution was lower than that in the single component solution in Figure 5.3 (a). The maximum loading of gold was in the range of 100 to 500 mg/l, which is equivalent to an upgrading ratio in the range of a 1000 to 5000. Maximum gold loading on the four respective resins, in decreasing order, was found to be as follows: Amberlite PWA-5 > Minix > Dowex 21K XLT > Amberjet 4600, which is different to what was previously found for the single component solution.

From Figure 5.4 (b), it can be observed that the maximum platinum loading achieved was lower than that in the single component solution in Figure 5.4 (b). The maximum loading of platinum was in the range of 130 to 580 mg/l, which is equivalent to an upgrading ratio in the range of 860 to 3870. Maximum platinum loading on the four resins, in decreasing order, was found to be as follows, Dowex 21K XLT > Amberlite PWA-5 > Amberjet 4600 > Minix, which is similar to that observed for the single component platinum solution.

From Figure 5.4 (c), it can again be seen that as with gold and platinum, the maximum

palladium loading achieved from a multicomponent solution was lower than that observed in the single component palladium solution. The maximum palladium loading is now in the range of 210 to 1250 mg/l, which is equivalent to an upgrading ratio range of 525 to 3125. Maximum palladium loading on the four resins, in decreasing order, was found to be as follows, Dowex 21K XLT > Amberlite PWA-5 > Amberjet 4600 > Minix, which is similar to that found for the single component palladium solution.



**Figure 5.5:** Isotherms for (a) zinc, (b) nickel), (c) copper and (d) iron for the 4 respective resins, generated from a multicomponent solution

Figure 5.5 represents the multicomponent isotherms of (a) zinc, (b) nickel, (c) copper and (d) iron for the four anion exchange resins. From Figure 5.5 (a) it can be seen that maximum zinc loadings of between 3700 and 13000 mg/l could be achieved with the four resins, from a multicomponent solution containing 5 ppm of zinc. The maximum zinc loading on the four resins, in decreasing order, was found to be as follows: Amberlite PWA-5 > Dowex 21K XLT > Amberjet 4600 > Minix.

From Figure 5.5 (b) it can be observed that maximum nickel loadings of between 1800 and 9800 mg/l could be achieved with the four resins, from a multicomponent solution containing 5 ppm of nickel. The maximum nickel loading on the four resins, in decreasing order was as follows, Amberlite PWA-5 > Dowex 21K XLT > Amberjet 4600 > Minix. A clustering of nickel isotherm points for Minix can be seen, which is an indication of

Minix having a low affinity for  $Ni(CN)_4^{2-}$ , because the loading on the resin is low and the concentration of nickel in solution at equilibrium is high, irrespective of the resin-to-solution ratio used.

In Figure 5.5 (c), it can be observed that maximum copper loadings of between 1000 and 9100 mg/l were achieved with the four resins, from a multicomponent solution containing 10 ppm of copper. The maximum copper loading on the four resins, in decreasing order, was found to be as follows, Amberjet 4600 > Amberlite PWA-5 > Dowex 21K XLT > Minix. Again a cluster of copper isotherm points was noticed for Minix, which indicated the low affinity of Minix for the  $Cu(CN)_4^{3-}$  anion.

From Figure 5.5 (d), it can be seen that maximum iron loadings of between 300 and 11000 mg/l could be achieved with the four resins, from a multicomponent solution containing 10 ppm of iron. The maximum iron loading on the four resins, in decreasing order, was found to be as follows, Amberjet 4600 > Dowex 21K XLT > Amberlite PWA-5 > Minix. Clusters of iron isotherm points can be observed for both Amberlite PWA-5 and Minix, which indicates the low affinity that these 2 resins have for the  $Fe(CN)_6^{4-}$  anion.

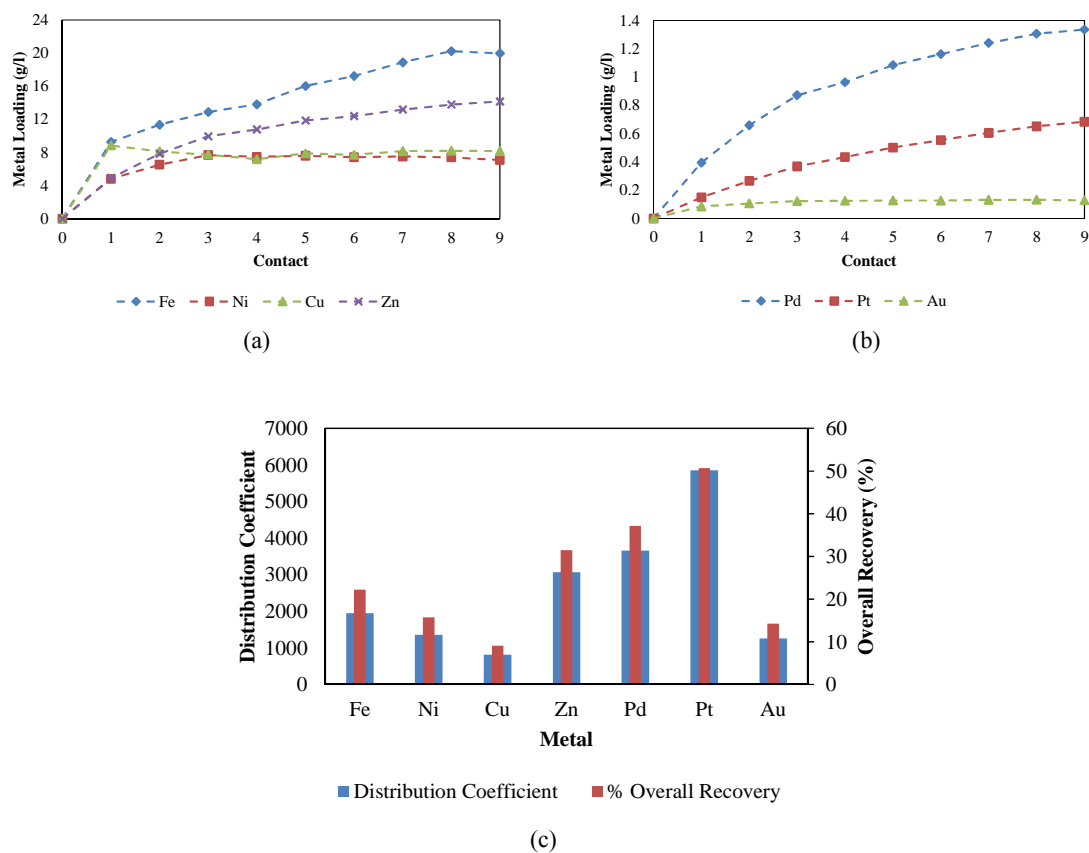
To summarize, large decreases in the maximum loadings achieved for platinum, palladium and gold onto all four resins were observed, going from single to multicomponent systems. The primary reason for this is that all the active sites on the resin are not available for any specific anion in multicomponent systems, but that they are occupied by quantities of all anions in solution. Thus the higher the affinity of the resins for a specific anion, the higher the maximum loading of that anion will be from a multicomponent solution.

When considering the base metals, all four resins showed high affinities for the  $Zn(CN)_4^{2-}$  anion, with maximum loadings of between 3700 and 13000 mg/l. Nickel also loaded significantly onto three of the resins, but was poorly loaded onto Minix. Relatively high copper loadings were achieved onto all resins, again with the exception of Minix that showed low affinity for the  $Cu(CN)_4^{3-}$  anion. Iron showed poor loadings onto both Minix and Amberlite PWA-5, but high iron loadings were achieved onto Amberjet 4600 and Dowex 21K XLT.

## 5.4 Repeated Batch Loading

Repeated batch loading experiments consisted of contacting fresh resin with the solution, shown in Table 5.1, for 24 hours, in a resin-to-solution ratio of 1:1000. The loaded resin was then vacuum-filtered from the solution, and re-introduced to fresh solution, after which the loading process was repeated. During each each contact, a sample of solution

after 24 hours was taken and analyzed for the metals present, from which a mass balance was performed to determine the loading of each metal on the resin. Loading profiles over the nine contacts performed could be generated for each resin, along with distribution coefficients at each contact as well as the overall recovery of each metal after the 9<sup>th</sup> contact. The loading profiles of the base metals and platinum, palladium and gold are presented separately, with the distribution coefficient of each metal at the 9<sup>th</sup> contact and the overall recovery of each metal presented on the same figure.



**Figure 5.6:** Repeated loading profiles onto Dowex 21K XLT of (a) base metals and (b) platinum, palladium and gold along with (c) the overall recoveries of metals and distribution coefficients of metals after contact 9

From Figure 5.6(a) it can be seen that large amounts of iron and zinc were loaded onto Dowex 21K XLT during the duration of the experiment, with moderate loadings of nickel and copper. The high base loading onto Dowex 21 K XLT was expected from the batch kinetic results of this resin. Iron achieved a loading of approximately 20 g/l, which comprised a substantial fraction of the total metal loading at the end of the experiment. From the base metal loading profiles, it can also be observed that the loading of copper and nickel did not increase after contacts one and three, respectively. The loading of iron and zinc increased throughout the duration of the experiment.



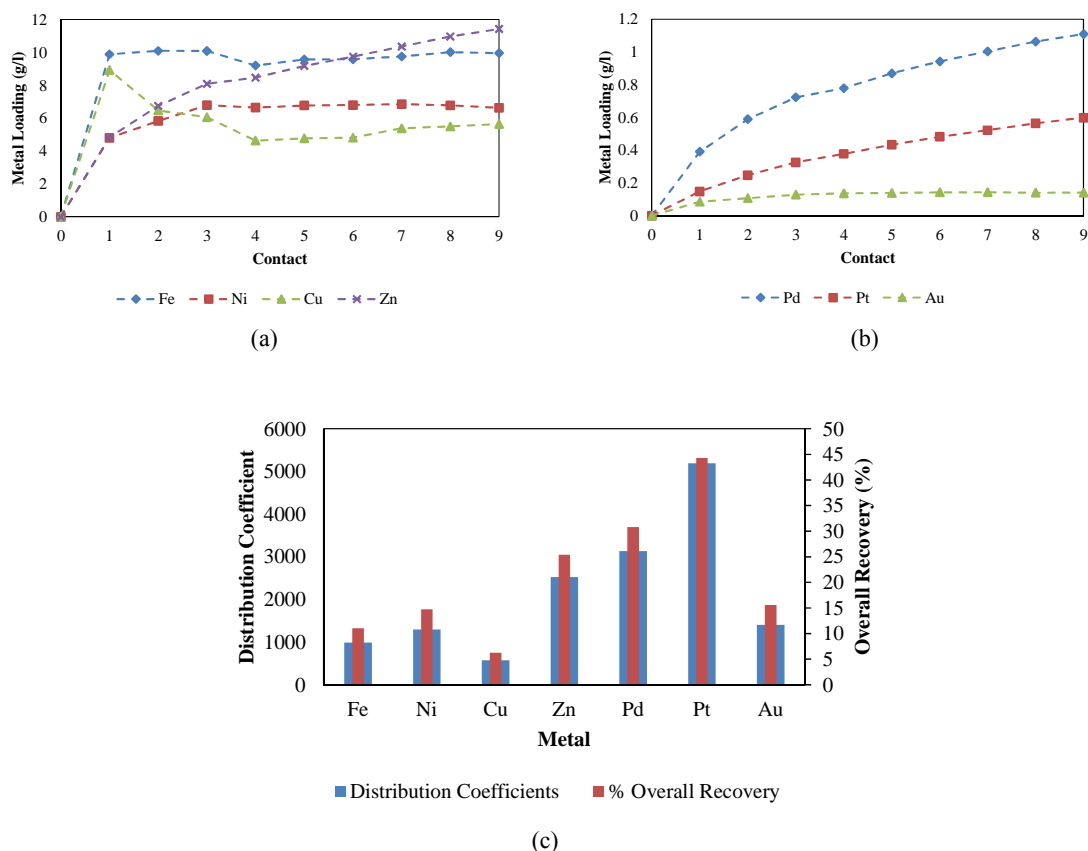
When comparing the loading profiles of the base metals in Figure 5.6 (a) with those of platinum, palladium and gold in Figure 5.6 (b), it is clear that the loadings of platinum, palladium and gold are an order of magnitude lower than those of the base metals, at the end of the experiment. As stated earlier, the reason for this can be attributed to the low concentrations of platinum, palladium and gold in the cyanide solution that are much lower than the base metal concentrations. From Figure 5.6 (b) it can be observed that the loading of platinum and palladium increased over the duration of the experiment with relatively high loadings of these two metals at the end of the experiment. The gold loading did not increase further after contact three, which resulted in a low gold loading.

After considering the distribution coefficient in Figure 5.6 (c) for each metal at the end experiment, a selectivity series for Dowex 21K XLT could be generated, as shown below:

$$\text{Pt} > \text{Pd} > \text{Zn} > \text{Fe} > \text{Ni} > \text{Au} > \text{Cu}$$

A similar selectivity series was generated by Riveros (1993), for Amberlite IRA-400, also a strong base anionic resin containing a tri-methyl functionality, with the exception of platinum and palladium that were not included in the study. However, although the selectivity series above suggests that Dowex 21K XLT has the highest affinity for platinum and palladium, their loadings are still low compared with those of the base metals. When looking at the overall recovery of each metal over the nine contacts, they could be related to the distribution coefficients of the metals. Platinum, which had the highest distribution coefficient, also had the highest overall recovery of just below 50%, with copper having the lowest overall recovery of just below 10% along with the lowest distribution coefficient.

Figure 5.7 represents the repeated batch loading results for Amberjet 4600. From Figure 5.7 (a) it can be seen that iron and zinc were the base metals with the highest loadings onto Amberjet 4600. The copper rejection after contact one could not be explained, but could be a result of the lower exchange capacity (1.25 eq/l) when compared with the exchange capacity (1.4 eq/l) of Dowex 21K XLT. Thus the zinc that increases in loading over the duration of the experiment is probably causing the copper to be rejected from the resin to a certain point, after which the copper loading stays relatively constant. As with Dowex 21K XLT in Figure 5.6 (a), the copper and nickel loadings on Amberjet 4600 at the completion of the experiment were similar. The results in Figure 5.6 (a) and Figure 5.7 (a) confirm the observation made in the batch kinetic results, which is that the high base metal loading potential of Dowex 21K XLT and Amberjet 4600 can create problems, when considering the low concentrations of platinum, palladium and gold in the cyanide solution.



**Figure 5.7:** Repeated loading profiles onto Amberjet 4600 of (a) base metals and (b) platinum, palladium and gold along with (c) the overall recoveries of metals and distribution coefficients of metals after contact 9

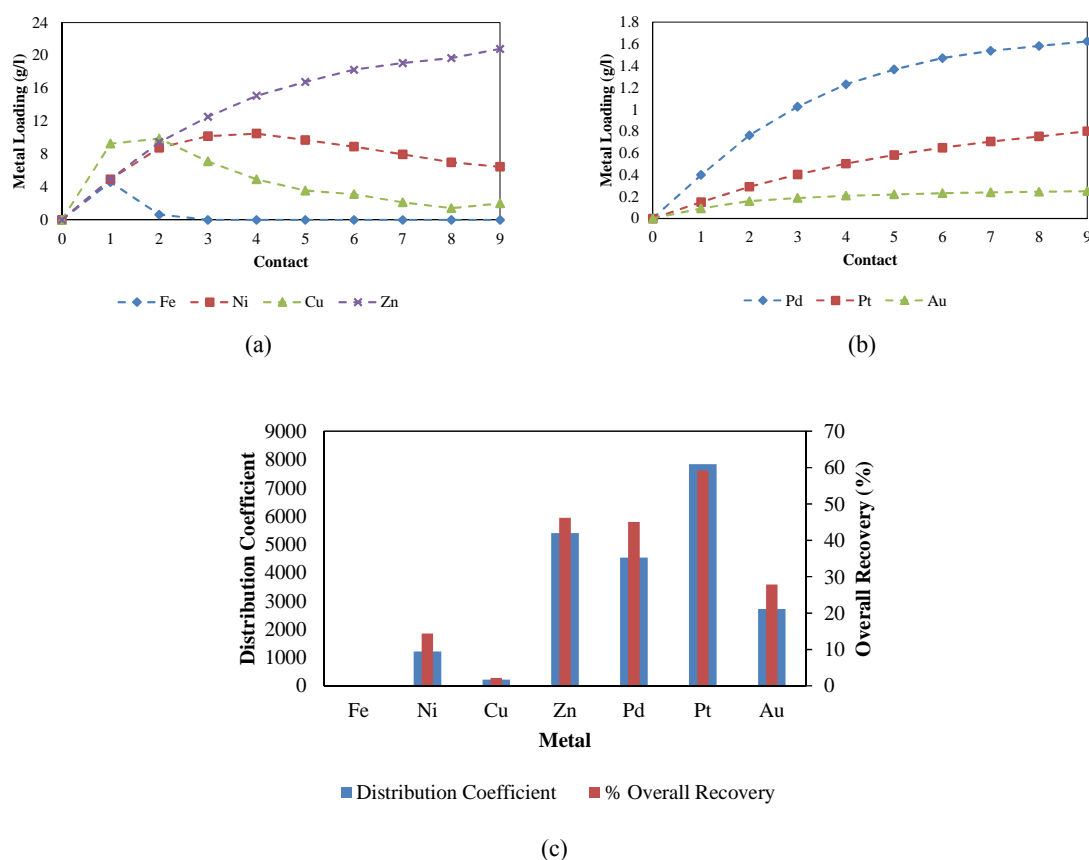
Again, as with Dowex 21K XLT, it can be seen that the loadings of platinum, palladium and gold in Figure 5.7 (b) are an order of magnitude lower than those of the base metals. The loading profiles of platinum, palladium and gold in Figure 5.7 (b) onto Amberjet 4600 are very similar to those of these metals onto Dowex 21K XLT in Figure 5.6 (b). This again confirms the similarity in loading between these two resins. The palladium loading on Amberjet 4600 was the highest, followed by platinum and then gold. However the palladium and platinum were the only two metals that increased in loading during the duration of the experiment, with the gold loading not increasing further after contact four.

When looking at the distribution coefficients of the metals in Figure 5.7 (c), a selectivity series for Amberjet could be generated, as is presented below:

$$\text{Pt} > \text{Pd} > \text{Zn} > \text{Au} > \text{Ni} > \text{Fe} > \text{Cu}$$

The affinity of Amberjet 4600 for iron and nickel is lower than the affinity of Dowex 21K XLT for these 2 metals. The affinity for gold is higher when Amberjet 4600 is used rather than Dowex 21K XLT. However, although iron is very low on the selectivity series

of Amberjet 4600, a significant amount of iron is still loaded on the resin at the end of the experiment. The loading of all metals also decreased with the use of Amberjet 4600, with no significant change in selectivity. Looking at the overall recoveries of the metals in Figure 5.7 (c), a decrease in all overall recoveries can be seen, when compared to the overall recoveries for Dowex 21K XLT in Figure 5.6 (c), with the exception of gold. The slight increase in the overall recovery of gold is however too low to deem this resin more effective than Dowex 21K XLT, especially with the loading of gold becoming stationary for both Dowex 21K XLT and Amberjet 4600. Again, as with Dowex 21K XLT it can be concluded that the overall recovery of metals is directly related to the affinity that the resin has for them.



**Figure 5.8:** Repeated loading profiles onto Amberlite PWA-5 of (a) base metals and (b) platinum, palladium and gold along with (c) the overall recoveries of metals and distribution coefficients of metals after contact 9

Figure 5.8 represents the repeated batch loading results for Amberlite PWA-5. From Figure 5.8 (a), a distinct difference in the loading profiles of the base metals can be noticed, when compared with the loading profiles of base metals onto Dowex 21K XLT and Amberjet 4600, in Figures 5.6 and 5.7, respectively. Iron, copper and nickel are rejected by Amberlite PWA-5 after contacts one, two and four, respectively. Zinc is the only base metal that continues to increase in loading during the duration of the experiment. Iron

is fully rejected, with partial rejection of copper and nickel. The lower exchange capacity and larger functionality of Amberlite PWA-5 will result in less sites being available for the tetra-valent iron cyanide complex, which in return will cause all the iron cyanide to be displaced by lower charged metal-cyanide complexes. The loading of zinc onto Amberlite PWA-5 at the end of the experiment, is much higher than onto Dowex 21K XLT and Amberjet 4600, with a decrease in the loading of nickel and copper.

From Figure 5.8 (b) it can be seen that the loadings of platinum, palladium and gold increased during the duration of the experiment. The loading of platinum, palladium and gold onto Amberlite PWA-5 was also higher than was obtained for Dowex 21K XLT and Amberjet 4600. Although the gold loading onto Amberlite PWA-5, increased at a much slower rate than that of platinum and palladium, no stationary gold loading phase was observed.

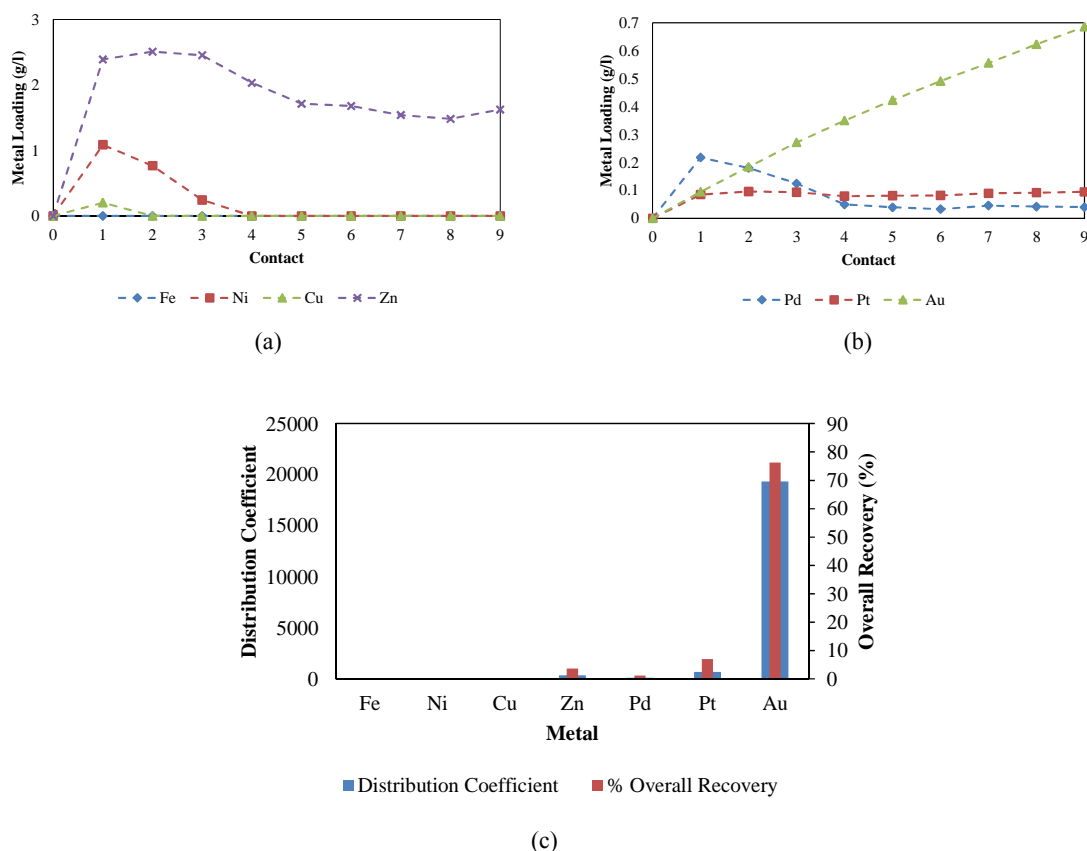
From the distribution coefficients of the metals in Figure 5.8 (c), a selectivity series for Amberlite PWA-5 could be generated, as presented below:



The selectivity series for Amberlite PWA-5 is similar to the selectivity series generated by Riveros (1993), with the use of Imac HP-555s, a strong base anionic resin containing a tri-ethyl functionality, with the exception of platinum and palladium, which were not included in the study. Amberlite PWA-5 has a very high affinity for platinum, palladium and gold, along with zinc as the only base metal present high up in the selectivity series. The selectivity series is different from the series generated for Dowex 21K XLT and Amberjet 4600, in the respect that Amberlite PWA-5 has a very low affinity for copper and iron, compared with the other metals in solution. The overall recoveries of all metals increased, with the exception of iron, copper, and nickel, which decreased in their overall recoveries, when compared to the overall recoveries for Dowex 21K XLT and Amberjet 4600.

Figure 5.9 shows the repeated batch loading results for Minix. From Figure 5.9 (a), a difference in base metal loading onto Minix can be observed, when compared with the base metal loading profiles of the three previous resins. All the base metals are rejected by Minix over the duration of the experiment. No loading could be observed for iron, nickel and copper after contact two and four respectively, with zinc only partially rejected. Thus at the end of the experiment, zinc was the only base metal still loaded onto Minix. The zinc loading however was much lower than previously observed onto Dowex 21K XLT, Amberjet 4600 and Amberlite PWA-5.

The loading profiles for platinum, palladium and gold in Figure 5.9 (b) are also significantly different to the loading profiles previously observed for these metals onto Dowex



**Figure 5.9:** Repeated loading profiles onto Minix of (a) base metals and (b) platinum, palladium and gold along with (c) the overall recoveries of metals and distribution coefficients of metals after contact 9

21K XLT, Amberjet 4600 and Amberlite PWA-5. Gold loading is increasing linearly over the duration of the experiment, with a final gold loading much higher than previously observed for the other three resins. Palladium is partially rejected after contact one, obtaining a low final loading onto Minix. Platinum increased in loading up to contact two, after which it reached a stationary loading phase that continued throughout the duration of the experiment.

From the distribution coefficients of the metals in Figure 5.9 (c), a selectivity series for Minix could be generated, which is presented below:

$$\text{Au} \gg \text{Pt} > \text{Zn} > \text{Pd} \gg \text{Ni} = \text{Cu} = \text{Fe}$$

From the selectivity series above, it can be concluded that Minix has a higher affinity for gold than for all other metals in solution, followed by the platinum, palladium and zinc, with very low affinity for nickel, copper and iron. In Figure 5.9 (c) it can be seen that the overall recoveries of the metals differ significantly from previous results. Gold obtained an overall recovery of above 65%, with very low or zero overall recoveries for all other metals present in solution.

**Table 5.8:** Loading of metals on resins, after the repeated loading experiment

Metal	Loading (g/l)			
	Dowex 21K XLT	Amberjet 4600 Cl	Amberlite PWA-5	Minix
Fe	20.0	10.0	-	-
Ni	7.1	6.6	6.5	-
Cu	8.2	5.6	2.0	-
Zn	14.2	11.4	20.8	1.6
Pd	1.3	1.1	1.6	0.0
Pt	0.7	0.6	0.8	0.1
Au	0.1	0.1	0.3	0.7
<b>Total</b>	<b>51.5</b>	<b>35.5</b>	<b>31.9</b>	<b>2.4</b>

**Table 5.9:** Fraction of platinum, palladium and gold on the resins after repeated loading experiment

Metal	Loading of Pt, Pd and Au (%)			
	Dowex 21K XLT	Amberjet 4600 Cl	Amberlite PWA-5	Minix
Pt	1.3	1.7	2.5	3.9
Pd	2.6	3.1	5.1	1.6
Au	0.2	0.4	0.8	28.1

Table 5.8 and Table 5.9 were generated to put the results of this section into perspective. The loading (g/l) of each metal as well as the total loading (g/l) of metals on each resin at the end of the experiment, along with the fractional loading (%) of platinum, palladium and gold with respect to the total metal loading on each resin, are shown. From Table 5.8, Dowex 21K XLT had the highest total metal loading (51.5 g/l) followed by Amberjet 4600 (35.5 g/l), Amberlite PWA-5 (31.9 g/l) and Minix (2.4 g/l). This decreasing order of total metal loading was expected, when considering the exchange capacities of the respective resins, represented in Table 5.2, in Section 5.1.

It can be observed from Table 5.8 that substantial amounts of base metals were loaded onto Dowex 21K XLT and Amberjet 4600, of which iron and zinc loadings were the highest in both cases. Platinum and palladium loadings were high, when considering the low concentrations of these metals in the solution. When observing the loading profiles and actual loading results of Dowex 21K XLT and Amberjet 4600 in Table 5.8, it can be seen that these two resins have a significant affinity for the di, tri and tetravalent complexes of  $Fe(CN)_6^{4-}$ ,  $Zn(CN)_4^{2-}$ ,  $Ni(CN)_4^{2-}$ ,  $Cu(CN)_4^{3-}$ ,  $Pt(CN)_4^{2-}$  and  $Pd(CN)_4^{2-}$ . The copper loading is not as high as the other base metals, and this could be a result of the copper forming different cyanide species in solution depending on the free cyanide concentration. The monovalent aurocyanide anion,  $Au(CN)_2^-$ , achieved poor loading (0.1 g/l), onto both Dowex 21K XLT and Amberjet 4600, which is due to the high

ionic densities of these two resins, which is selective for more highly charged anions than for lowly charged anions such as,  $Au(CN)_2^-$ . The gold was not rejected, it reached a stationary loading phase. A possible reason for this is that the two resins were not loaded nearly to full capacity, and thus it can be expected that the  $Au(CN)_2^-$  complex will be the first one to be rejected as the resin becomes more loaded. When looking at the fractional loading percentages of platinum, palladium and gold on Dowex 21K XLT and Amberjet 4600, respectively, in Table 5.9, palladium achieved the highest fractional loading percentages of 2.6% and 3.1%, followed by platinum, 1.3% and 1.7%, and gold, 0.2% and 0.4%. It is evident that the platinum, palladium and gold make up only a small fraction of the metals loaded onto these resins, which is again a direct result of their concentrations in the cyanide solution.

The loading results for Amberlite PWA-5 in Table 5.8 are significantly different from those for Dowex 21K XLT and Amberjet 4600. Base metal loadings were still high but iron was not the metal that constituted the highest fraction of these group of metals, but rather zinc, achieving a loading of 20.8 g/l. Amberlite PWA-5 showed a high affinity for the mono- and divalent anions of  $Zn(CN)_4^{2-}$ ,  $Ni(CN)_4^{2-}$ ,  $Pt(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$  and  $Au(CN)_2^-$ , with a low affinity for  $Cu(CN)_4^{3-}$  and  $Fe(CN)_6^{4-}$ . A small amount of copper was however present on the resin, which is believed to be the  $Cu(CN)_3^{-2}$  complex rather than the  $Cu(CN)_4^{3-}$  complex, which will also be present in the solution. The poor iron loading can be explained, in terms of the larger tri-ethyl functional group of Amberlite PWA-5. The functionality will sterically hinder the adsorption of the large tetravalent  $Fe(CN)_6^{4-}$  anion, and the lower exchange capacity (1 eq/l) will also make the adsorption of the  $Fe(CN)_6^{4-}$  anion difficult, because of the active groups spread further from each other, than in the cases of Dowex 21K XLT and Amberjet 4600. When observing the fractional loading percentages of platinum, palladium and gold in Table 5.9, it can also be seen that the percentages for all three these metals are higher when compared to the results of Dowex 21K XLT and Amberjet 4600. Palladium now constitutes 5.1% of the total metal loading followed by platinum constituting 2.5% and gold constituting 0.8%.

From Table 5.8, it can be seen, as with the loading profiles, that no base metals except for zinc (1.6 g/l), were present on Minix at the end of the experiment. Platinum and palladium loadings of 0.1 g/l and 0.04 g/l respectively, were very poor. The gold loading of 0.7 g/l onto Minix was the highest gold loading obtained for all four resins tested. Thus Minix proved to be very selective for the monovalent  $Au(CN)_2^-$  complex, that could easily load onto any active site. However, the low exchange capacity (0.3 eq/l) of Minix, and large tri-butyl functionality complicated the adsorption of the other multivalent complexes present in solution. Some divalent anions, such as  $Pt(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$  and  $Zn(CN)_4^{2-}$  were able to achieve low loadings onto Minix, the reason

being that these divalent anions were less affected by the lower exchange capacity and larger functionality. Other complexes such as  $Cu(CN)_4^{3-}$  and  $Fe(CN)_6^{4-}$ , cannot load effectively on Minix with its low ionic density and large functional groups, because the complexes cannot find enough active groups to adsorb on, and also the tri-butyl groups sterically hinder their adsorption. Regarding the fraction loading percentages of platinum, palladium and gold in Table 5.9, platinum constituted 0.1%, with palladium constituting 0.05% and gold constituting 28.1% of the total metal loading. This high fractional loading of gold onto Minix, again confirms the high affinity that Minix has for the monovalent aurocyanide anion.

## 5.5 The Effect of Different Parameters on Adsorption

After considering all previous results a decision was made to continue tests with only Amberlite PWA-5 and Minix. These two strong base anionic resins had the highest platinum, palladium and/or gold loading potential, with the lowest base metal loading potential. Dowex 21K XLT and Amberjet 4600, adsorbed all metals in a non-selective manner, which resulted in high base metals as well as high platinum, palladium and gold loadings. Another disadvantage of these two anionic exchange resins, is the high iron loading that could affect the downstream elution process negatively. The reason for this is the strong bonding of  $Fe(CN)_6^{4-}$  to the resin, because of the high stability of the metal cyanide complex, which will result in a similar bonding strength as those of  $Pt(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$  and  $Au(CN)_2^-$ , which are also very stable complexes. Thus when eluting platinum, palladium and gold from the resin, the iron will also be present in the eluate, because it will be eluted at the same conditions. The complexes of  $Zn(CN)_4^{2-}$ ,  $Ni(CN)_4^{2-}$ ,  $Cu(CN)_4^{3-}$  and  $Cu(CN)_3^{2-}$  are all weak acid dissociable complexes, and could thus theoretically be eluted with a weak acid before the elution of platinum, palladium and gold. They would thus not have such a large impact on the downstream elution process, as iron.

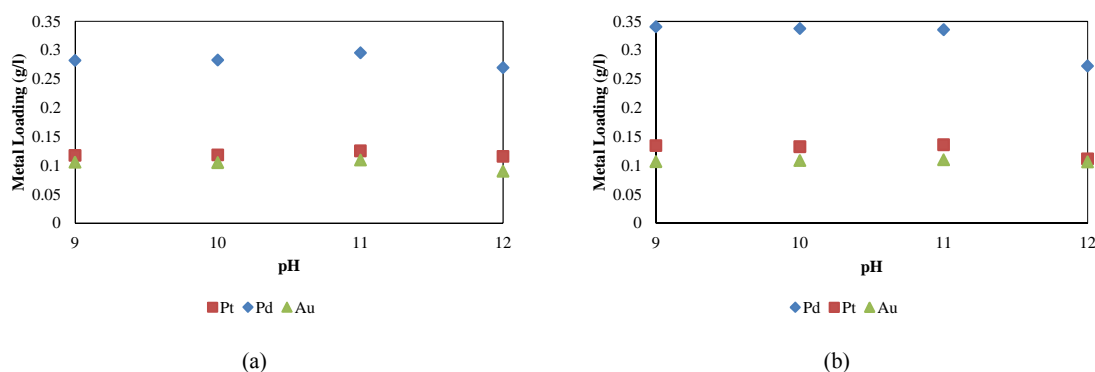
The experiments presented and discussed in this section, involved investigating the effect of pH, temperature, base metal concentration and platinum, palladium and gold concentrations, primarily on the adsorption of platinum, palladium and gold onto Amberlite PWA-5 and Minix. The experiments were done in a batch wise manner, contacting resin with solutions for 48 hours at a time.

### 5.5.1 The Effect of pH

The adsorption of metals from the solution in Table 5.1, at different pH values of 9, 10, 11 and 12 onto Amberlite PWA-5 and Minix was investigated. The experiments were performed in rolling bottles, using a resin-to-solution ratio of 1: 1000 over a 48 hour



period. Samples were collected at the beginning and the end of each experiment and analyzed for the respective metals, from which the loading of each metal was calculated using a mass balance. The pH at the beginning and end of each experiment was also measured and no pH change was observed in any of the experiments performed.

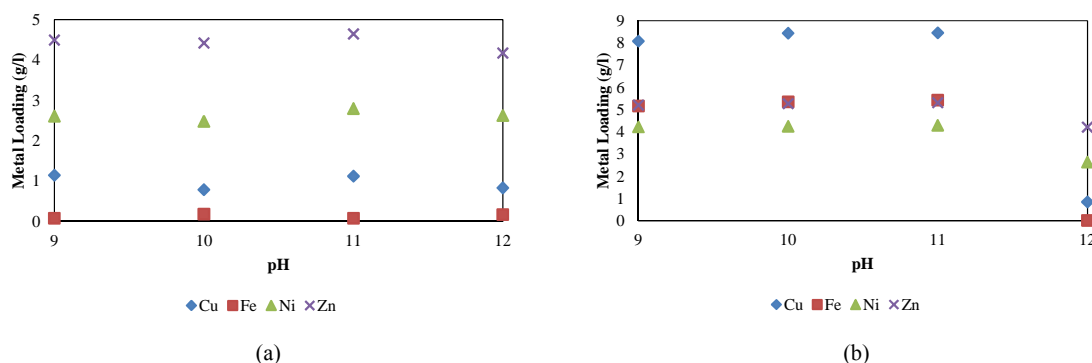


**Figure 5.10:** Effect of pH on the loading of platinum, palladium and gold onto (a) Minix and (b) Amberlite PWA-5

Figure 5.10, shows the loading of platinum, palladium and gold at different pH values onto Amberlite PWA-5 and Minix. From Figure 5.10 (a) it can be seen that the loading of platinum, palladium and gold onto Minix stayed relatively constant over the entire pH range tested. It can be concluded that pH did not have a major effect on the loading of platinum, palladium and gold onto Minix.

However it can be seen from Figure 5.10 (b) that the loading of platinum and palladium was affected by the pH of the solution. The loading of both platinum and palladium stayed relatively constant in the pH range, 9 - 11, however a drop in the loading was observed for both these metals at pH 12. Decreases of 18% and 19% in platinum and palladium loading respectively were observed, from pH 11 to pH 12. These decreases in loading could not be explained in terms of the hydroxide concentration in the solutions, because the pH stayed constant during the experiments, and thus the available sites on the resin were not occupied by hydroxide ions. The reason that the pH effect was observed only for Amberlite PWA-5 and not for Minix, can also not be explained. No literature could be found that supported this finding. Gold loading however stayed relatively constant over the entire pH range tested.

Figure 5.11, shows the loading of base metals at different pH values onto Amberlite PWA-5 and Minix. From Figure 5.11 (a) it can be seen that the base metal loading onto Minix, stayed relatively constant at all pH values. This result confirms the observation made in Figure 5.10 (a), that pH has little affect on the loading of metal cyanides onto Minix.



**Figure 5.11:** Effect of pH on the loading of base metals onto (a) Minix and (b) Amberlite PWA-5

It can be seen in Figure 5.11 (b) that the loadings of base metals onto Amberlite PWA-5 were affected by the pH of the solution. The loading of all base metals stayed relatively constant throughout the pH range, 9 to 11, after which a decrease in the loading of all base metals was observed from pH 11 to 12. Nickel and zinc loading decreased by 39% and 21%, respectively, whereas copper and iron loading was decreased by 90% and 100%, respectively, from pH 11 to 12. Thus the same decreasing trend in loading that was observed for platinum and palladium in Figure 5.10 (b), was also observed for the base metals. The decrease in loading of base metals, however, was much more severe than for platinum and palladium, and could be due to the large concentration difference between platinum and palladium and the base metals in the cyanide solution.

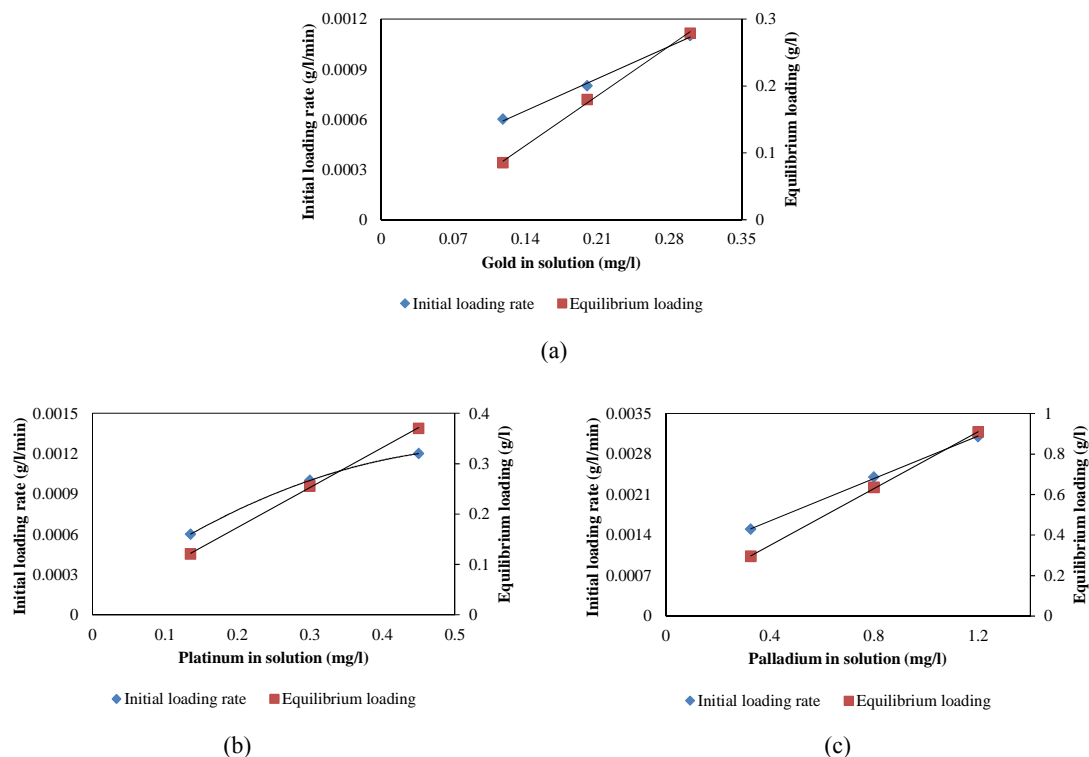
A reason for the large effect of pH on the loading of Amberlite PWA-5 and not Minix could not be found. From the results of Amberlite PWA-5 it can be seen that the gold loading was not affected by the pH, whereas platinum, palladium, zinc and nickel loading were much less affected by the pH, than iron and copper. If the cyanide complexes of these metals are considered, then the loading of the monovalent,  $Au(CN)_2^-$  anion, onto Amberlite PWA-5 was the least affected by pH, followed by the divalent anions of  $Pt(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$ ,  $Zn(CN)_4^{2-}$  and  $Ni(CN)_4^{2-}$ , with the tri- and tetravalent anions of  $Cu(CN)_4^{3-}$  and  $Fe(CN)_6^{4-}$  being the most affected by pH. The reason for the copper being less affected than the iron could be due to a fraction of the copper being present in its divalent form as  $Cu(CN)_3^{-2}$ , which will then behave similarly to the divalent cyanide complexes of platinum, palladium, zinc and nickel. This observation could indicate that an exchange capacity reduction or functional group modification of Amberlite PWA-5 occurred at pH 12 that restricted the loading of highly charged anions.

### 5.5.2 The Effect of the Concentration of Platinum, Palladium and Gold

The investigation was performed using the solution composition presented in Table 5.3, and only increasing the concentrations of platinum, palladium and gold in solution. The experiments were performed in rolling bottles, over a 48 hour period, using a resin-to-solution ratio of 1:1000, in the cases of both Minix and Amberlite PWA-5. Pre-determined times were used to collect samples, to calculate the initial loading rates of the metals, as well as the final loading of each metal at equilibrium. Loading and initial loading rate profiles could then be generated for each of the resins. The concentrations of platinum, palladium and gold used during each experiment are shown in Table 5.10.

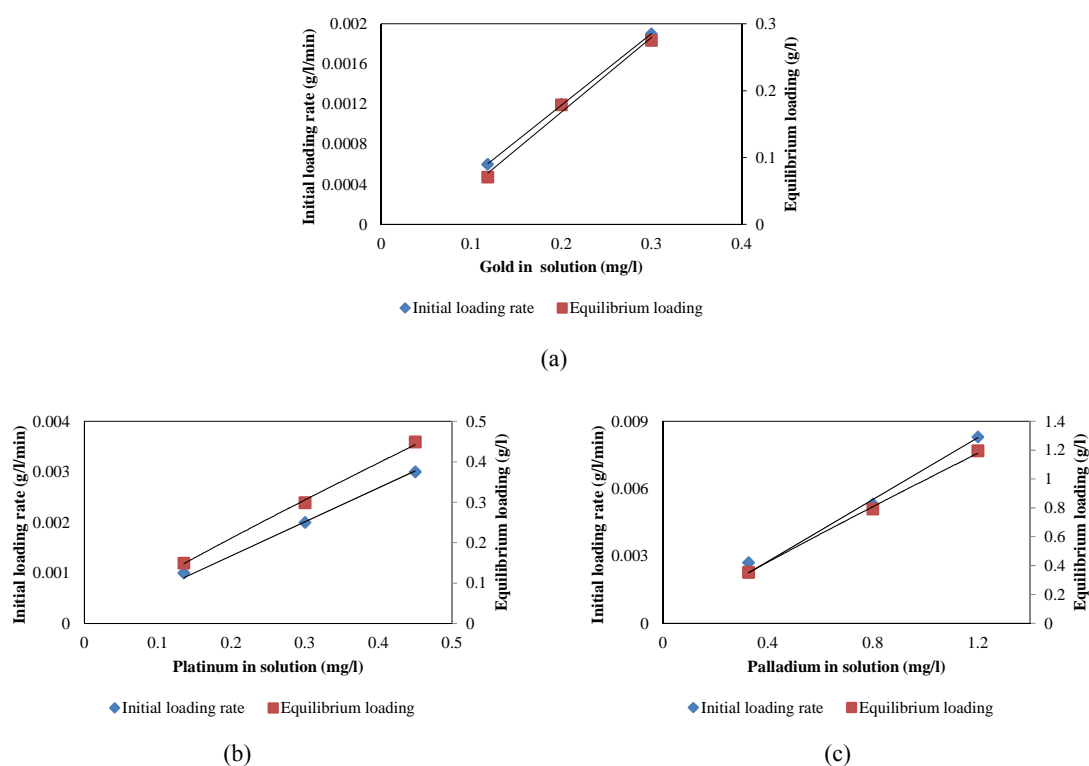
**Table 5.10:** Concentrations of metals used in each experiment

Nr.	Concentration (mg/l)		
	Au	Pt	Pd
1	0.10	0.15	0.40
2	0.20	0.30	0.80
3	0.30	0.45	1.20



**Figure 5.12:** Loading and kinetic profiles for (a) gold, (b) platinum and (c) palladium onto Minix

Figure 5.12 shows the equilibrium loading and initial loading rate profiles for the adsorption of platinum, palladium and gold onto Minix. From Figure 5.12 (a), it can be seen that both the equilibrium loading and initial loading rate of gold increased with an increasing concentration of gold in solution. Similar trends to that of gold in both the equilibrium loadings and initial loading rates of platinum and palladium can be observed in Figures 5.12 (b) and (c). However, the initial loading rate of platinum with increasing concentration, was not linear, as was observed for gold and palladium. Increasing the metal concentration of each metal to three times the concentration represented in Table 5.3, increased palladium loading by 0.6 g/l, the platinum loading by 0.27 g/l and the gold loading by 0.2 g/l.



**Figure 5.13:** Loading and kinetic profiles for (a) gold, (b) platinum and (c) palladium onto Amberlite PWA-5

Figure 5.13, shows the equilibrium loading and initial loading rate profiles for the adsorption of platinum, palladium and gold onto Amberlite PWA-5. From Figures 5.13 (a), (b) and (c), it can be seen that linear increases in both the equilibrium loadings and initial loading rates of gold, platinum and palladium were achieved with increases in their concentrations in the feed solution. Increasing the concentration of the metals to three times their concentrations in the original solution, increased the palladium loading by 0.85 g/l, the platinum loading by 0.3 g/l and the gold loading by 0.2 g/l.

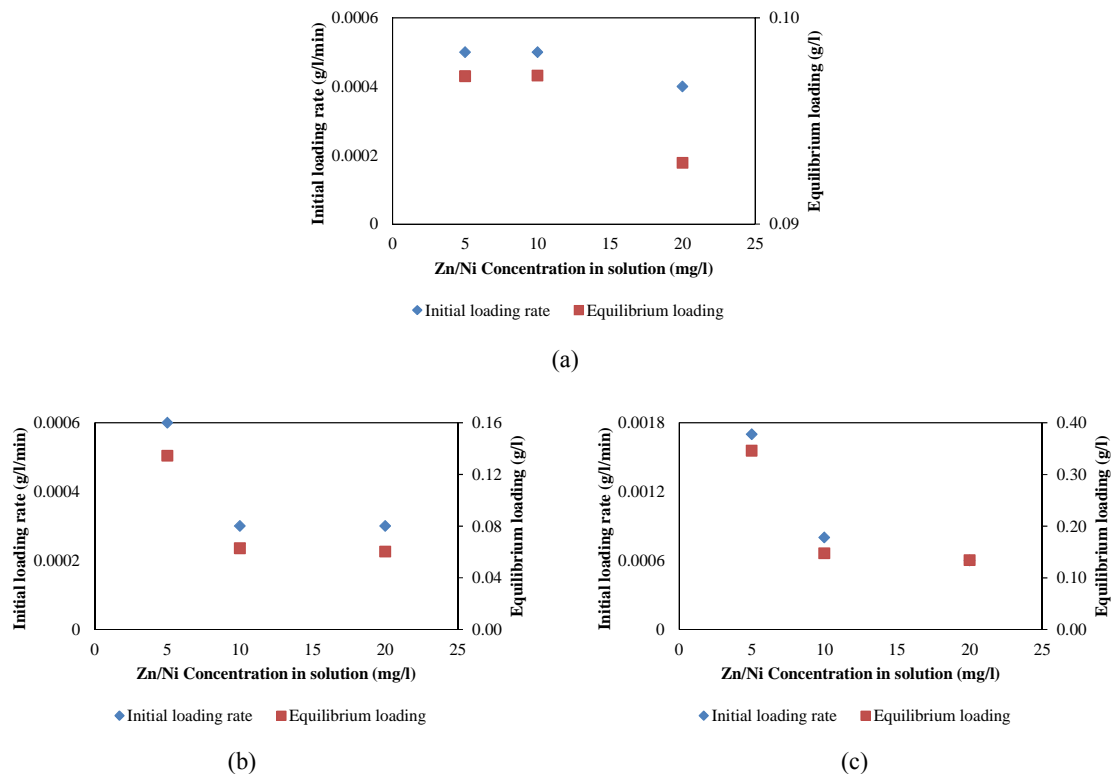
From these results, it is clear that the loading and initial loading rate of platinum, palladium and gold onto both Minix and Amberlite PWA-5, can be improved significantly, when their concentrations in the feed solution are increased. The reason is probably the increased frequency of contacts between anions and active sites in the case of higher concentrations. Since the solution at this point is very dilute in platinum, palladium and gold, an increase in their concentrations could significantly improve the kinetics and recovery of metals from solution, on an industrial scale.

### 5.5.3 The Effect of Base Metal Concentration

It was observed from previous results that considerably high amounts of nickel and zinc were loaded onto both Minix and Amberlite PWA-5. The reason for this is that  $Zn(CN)_4^{2-}$  and  $Ni(CN)_4^{2-}$  are similar complexes to  $Pt(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$  and  $Au(CN)_2^-$ , which gives them similar adsorption kinetics. It was discussed previously that  $Cu(CN)_4^{3-}$  and  $Fe(CN)_6^{4-}$  loaded poorly onto both these resins, the reason being the lower exchange capacities and larger functional groups of Minix and Amberlite PWA-5. It was then decided to only investigate the effect of nickel and zinc on the adsorption of platinum, palladium and gold from the cyanide solution.

The investigation was performed using concentrations of platinum, palladium and gold similar to those expected in the pregnant leach solution, namely, 0.15 ppm, 0.4 ppm and 0.1 ppm, respectively. Equal amounts of copper and nickel were then added to the solutions, to provide concentrations of these metals in solution of between 5 and 20 ppm. The experiments were performed on rollers, with the solutions having a pH of 10.5, for 48 hours. Samples were collected at pre-determined time intervals, and analyzed by ICP-MS. The results were then used to calculate the initial loading rates and equilibrium loadings of gold, platinum and palladium, at the different zinc/nickel concentrations.

From Figure 5.14 (a) it can be seen that the loading of gold on Minix was not affected by the zinc and nickel concentrations in solution, over the entire concentration range investigated. From Figures 5.14 (b) and (c) it can be seen that the loadings of platinum and palladium on Minix were significantly affected by the concentrations of zinc and nickel in solution. A 0.2g/l and 0.06 g/l decrease in loading was observed for palladium and platinum respectively, as the concentrations of nickel and zinc in solution were increased from 5mg/l to 10 mg/l. However, no significant decrease in loading of platinum and palladium was observed when the concentrations of nickel and zinc were increased to 20mg/l. From the Figures 5.14 (a), (b) and (c) it can be seen that the initial loading rates of gold, platinum and palladium are affected by the concentrations of nickel and zinc in the cyanide solution. The initial loading rate of gold was not affected by the concentrations of nickel and zinc, up to 10 mg/l, after which a 25% decrease was observed as the concentrations

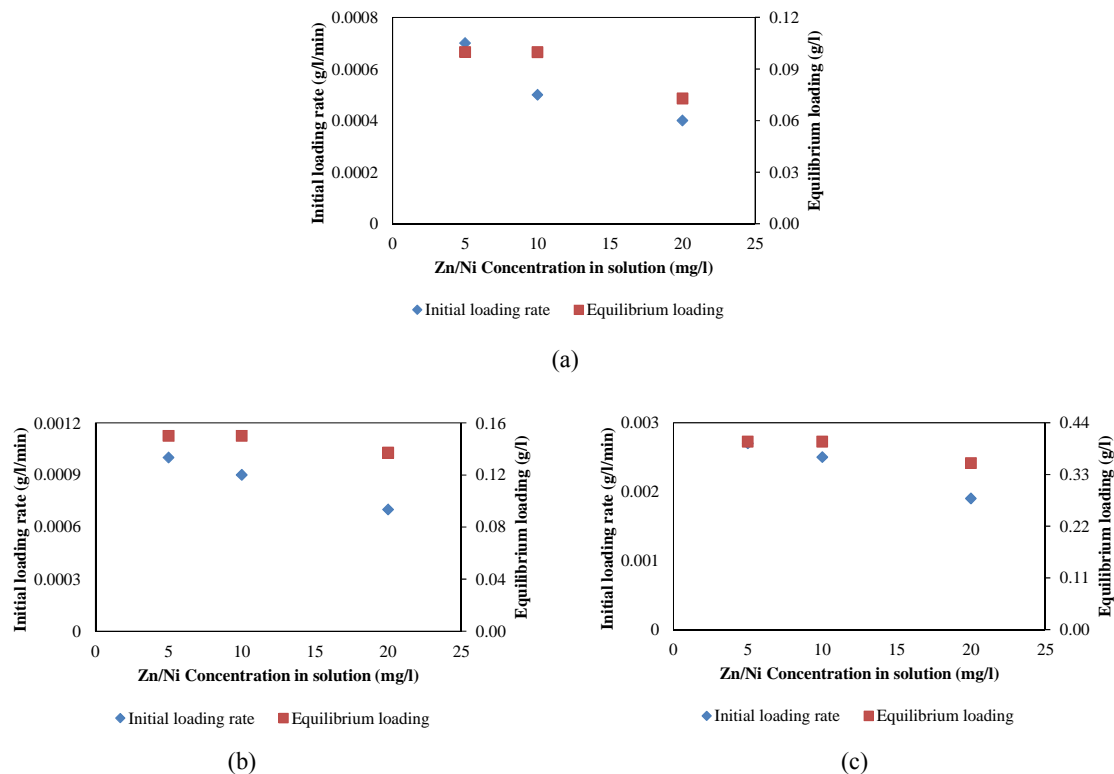


**Figure 5.14:** The effect of zinc and nickel concentration on the loading and loading rate of (a) gold, (b) platinum and (c) palladium onto Minix

were increased to 20 mg/l. The initial loading rate of platinum decreased by 100%, from 5mg/l to 10 mg/l of nickel and zinc in solution, however no further decrease in the initial loading rate of platinum was observed when the concentrations were increased to above 10mg/l. A sharp decrease of 112% in the initial loading rate of platinum was observed when the nickel and zinc concentration was increased from 5mg/l to 10mg/l. The initial loading rate of palladium decreased a further 33% when the concentrations of nickel and zinc were increased to 20 mg/l.

From Figures 5.15 (a), (b) and (c), it can be seen that the loadings of platinum, palladium and gold onto Amberlite PWA-5 were constant up to a concentration of 10 mg/l of nickel and zinc in the cyanide solution. However, slight decreases in the loading of all three metals, 0.05 g/l for palladium, 0.02 g/l for platinum and 0.03 g/l for gold, were observed as the nickel and zinc concentrations were increased to 20 mg/l in solution.

The initial loading rates of platinum, palladium and gold onto Amberlite PWA-5, presented in Figures 5.15 (a), (b) and (c), decreased linearly as the concentrations of zinc and nickel were increased from 5 mg/l to 20 mg/l in the solution. Total decreases in initial loading rates of 42 % for palladium, 42 % for platinum and 35 % for gold onto Amberlite PWA-5, were observed as the zinc and nickel concentrations in solution were increased from 5 mg/l to 20 mg/l.



**Figure 5.15:** The effect of zinc and nickel concentration on the loading and loading rate of (a) gold, (b) platinum and (c) palladium onto Amberlite PWA-5

From the results it is clear that the recovery of  $Au(CN)_2^-$  by Minix is not significantly affected by the concentration of  $Zn(CN)_4^{2-}$  and  $Ni(CN)_4^{2-}$ , compared with the recovery of  $Pt(CN)_4^{2-}$  and  $Pd(CN)_4^{2-}$ . The main reason for this is the fact that  $Pt(CN)_4^{2-}$  and  $Pd(CN)_4^{2-}$  complexes, are similar complexes to those of  $Zn(CN)_4^{2-}$  and  $Ni(CN)_4^{2-}$ , and thus are affected more than the monovalent  $Au(CN)_2^-$  complex. The low exchange capacity and large tri-butyl functionality of Minix will also make it difficult for  $Zn(CN)_4^{2-}$  and  $Ni(CN)_4^{2-}$  anions to adsorb, even if present in large concentrations.

$Pt(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$  recoveries using Amberlite PWA-5, however, were less affected by the concentrations of  $Zn(CN)_4^{2-}$  and  $Ni(CN)_4^{2-}$  in solution. In the case of  $Au(CN)_2^-$  recovery, the recovery of the anion was affected by the concentrations of  $Zn(CN)_4^{2-}$  and  $Ni(CN)_4^{2-}$ , which was not observed for Minix. The reason for  $Pt(CN)_4^{2-}$  and  $Pd(CN)_4^{2-}$  recovery being less affected by the base metal concentration, can be ascribed to the higher exchange capacity and smaller tri-ethyl functionality of Amberlite PWA-5. Gold recovery however was affected by the concentration of zinc and nickel using Amberlite PWA-5, because of the resin's high affinity for divalent anions compared to that for monovalent anions.

### 5.5.4 The Effect of Temperature

During this investigation, the effect of temperature on the adsorption of platinum, palladium and gold was investigated. This was done because the cyanide heap leach can be performed using solar heating to improve the dissolution of platinum during leaching (Eksteen *et al.*, 2012). Either Minix or Amberlite PWA-5 was contacted with solution containing 5 ppm of each metal with a free cyanide concentration of 150 ppm at pH 10.5, in a resin-to-solution ratio of 1 : 1000. Each contact was performed at a different temperature, with the temperature ranging from 30°C to 60°C. The experiments were performed for 24 hours, which was sufficient for equilibrium to be reached in each case, with sampling of the solution at pre-determined time intervals during each experiment. The samples were analyzed with ICP-MS, and the analysis was used to calculate final loadings, initial loading rates and first order rate constants for platinum, palladium and gold at different temperatures.

**Table 5.11:** Loading and kinetic data for the effect of temperature on the recovery of platinum, palladium and gold onto Minix

Loading (g/l)			
Temperature (°C)	Pd	Pt	Au
30	5.83	5.28	5.48
40	5.83	5.28	5.48
50	5.83	5.28	5.48
60	5.83	5.28	5.48
Initial Loading Rate (g/l/min)			
Temperature (°C)	Pd	Pt	Au
30	0.075	0.064	0.048
40	0.077	0.067	0.054
50	0.081	0.071	0.062
60	0.084	0.074	0.067
First Order Rate Constants (min <sup>-1</sup> )			
Temperature (°C)	Pd	Pt	Au
30	0.023	0.022	0.014
40	0.027	0.026	0.015
50	0.031	0.029	0.019
60	0.036	0.034	0.023

Table 5.11 shows the loading and kinetic data for platinum, palladium and gold at



different temperatures for Minix. From Table 5.11, it can be seen that temperature did not affect the loading of metals, with constant loadings for platinum, palladium and gold over the temperature range investigated. A first order kinetic model was then fitted to the data, with  $R^2$  above 0.98 for all fitted data, which indicated that the loading of the metals at different temperatures could be described well by first order kinetics. Although the loading of the metals was not affected by temperature, the kinetics of adsorption of all metals was affected to some degree. Slight increases in both the initial loading rate and first order rate constant for all the metals were observed, as the temperature of the solution was increased from 30°C to 60°C.

**Table 5.12:** Loading and kinetic data for the effect of temperature on the recovery of platinum, palladium and gold onto Amberlite PWA-5

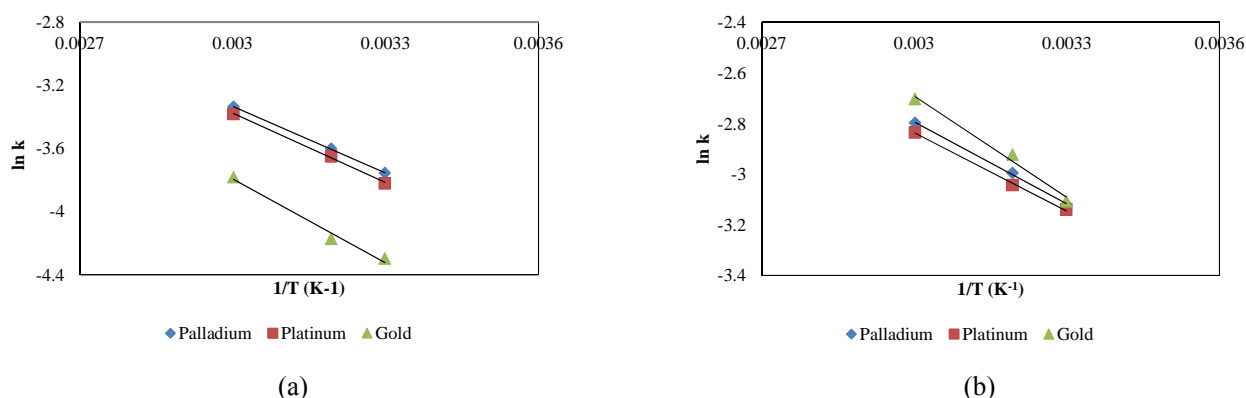
Loading (g/l)			
Temperature (°C)	Pd	Pt	Au
30	5.83	5.28	5.48
40	5.83	5.28	5.48
50	5.83	5.28	5.48
60	5.83	5.28	5.48
Initial Loading Rate (g/l/min)			
Temperature (°C)	Pd	Pt	Au
30	0.090	0.080	0.085
40	0.093	0.083	0.087
50	0.093	0.083	0.088
60	0.094	0.084	0.089
First Order Rate Constants (min <sup>-1</sup> )			
Temperature (°C)	Pd	Pt	Au
30	0.044	0.043	0.045
40	0.050	0.048	0.054
50	0.053	0.051	0.055
60	0.061	0.059	0.067

Table 5.12 shows the loading and kinetic data for platinum, palladium and gold for Amberlite PWA-5. Again as with Minix, it can be seen that temperature did not have an effect on the equilibrium loading of metals onto Amberlite PWA-5 up to 60°C. A first order kinetic model was fitted to the data, with  $R^2$  values above 0.98 for all fitted data, which indicated that the loading of metals onto Amberlite PWA-5 at different temperatures can be described well by first order kinetics. As with Minix when looking at the initial

loading rates and first order kinetic constants of the metals, it can be seen from Table 5.12 that the kinetics of loading improved as the temperature of the solution was increased. Increases in both the initial loading rate and first order rate constant were observed for all metals, when the temperature was increased from 30°C to 60°C.

An Arrhenius plot of the first order rate constants (as  $\ln k$ ) against temperature ( $1/T$ ), as shown in Figures 5.16, revealed activation energies for each metal on both Minix and Amberlite PWA-5, as shown in Table 5.13, and according to Equation 5.13:

$$\ln k = \ln A - \frac{E_a}{2.303RT} \quad (5.5.1)$$



**Figure 5.16:** Arrhenius plots for (a) Minix and (b) Amberlite PWA-5

**Table 5.13:** Activation energies for platinum, palladium and gold

Resin	Activation Energy (kJ/mol)		
	Pd	Pt	Au
Minix	27.0	28.2	34.0
Amberlite PWA-5	20.7	19.7	25.6

The activation energies presented in Table 5.13 for platinum, palladium and gold, confirm the increase in initial loading rate with increasing temperature. The activation energies for gold are also of the same order of magnitude as those obtained by Fleming and Cromberge (1984) for Amberlite IRA 400 of 16.5 kJ/mol. From Table 5.13, it can also be seen that the activation energies of platinum, palladium and gold for Minix are higher than the activation energies for Amberlite PWA-5. A possible reason for this is the difference in functionality and exchange capacities between the two resins. Minix contains a tri-butyl functionality with an exchange capacity of approximately 0.3 eq/l, whereas Amberlite PWA-5 contains a tri-ethyl functionality with an exchange capacity of 1.0 eq/l. This

will result in Minix being more sterically hindered due its larger functionality and lower exchange capacity, with respect to Amberlite PWA-5, which will result in Minix having higher activation energies. This is also the reason why the activation energy obtained by Fleming and Cromberge (1984), is lower than the activation energies obtained in this study. Both Minix and Amberlite PWA-5 are more sterically hindered than Amberlite IRA 400 that contains a trimethyl functionality with an exchange capacity of 1.4 eq/l.

In a study by Inglezakis and Zorpas (2012), it was concluded that activation energies of between 20 kJ/mol and 40 kJ/mol during adsorption of ions onto resins were a direct result of an ion exchange reaction taking place. Thus from the activation energies shown in Table 5.13, it can be deduced that the mechanism involved during the adsorption of these metal anions onto the respective resins were pure ion exchange, and not physisorption or chemisorption.

## Chapter 6

# Elution: Results and Discussion

The elution of metals from ion exchange resins was performed in glass columns, with water jackets to control the temperature within the columns. The resins were pre-loaded in bottles on rollers for 24 hours, which was determined to be sufficient to reach equilibrium. The first elution experiments involved loading Amberlite PWA-5 and Minix with solutions containing only gold, platinum and palladium, and then eluting these resins with acidic thiourea, zinc cyanide and thiocyanate, respectively, using the optimal conditions described in literature for the elution of aurocyanide. From these experiments, eluate concentration profiles as well as elution profiles, could be generated for all three eluting agents for both Minix and Amberlite PWA-5.

Secondly the effect of different parameters, such as flowrate, temperature and concentration, on the elution efficiency of all three eluting agents was investigated. In this experiment, only the elution from Amberlite PWA-5 was considered, where the resin was loaded in the same manner described previously, for the elution screening. The optimal conditions for each eluting agent were used during the investigation, only changing one parameter at a time for each experiment. From the elution profiles 15 bed volumes of eluate were determined to be sufficient to observe the effect of each parameter on the elution efficiency, and thus this amount was collected for each experiment.

### 6.1 Screening Eluting Agents

The resins used for this experiment were loaded by contacting the resins with a solution containing platinum, palladium and gold, in rolling bottles for 48 hours. After 48 hours the loaded resins were separated from the solution, via filtration, with samples taken before and after each loading for ICP-OES analysis, after which the loading on the resins could be determined by mass balance. The average loading of the metals, on both Minix and Amberlite PWA-5 was similar, and is shown in Table 6.1.

**Table 6.1:** Metal loading on resin for screening

Metal Loading (mg/l)		
Au	Pt	Pd
3966.	2784.	3316.

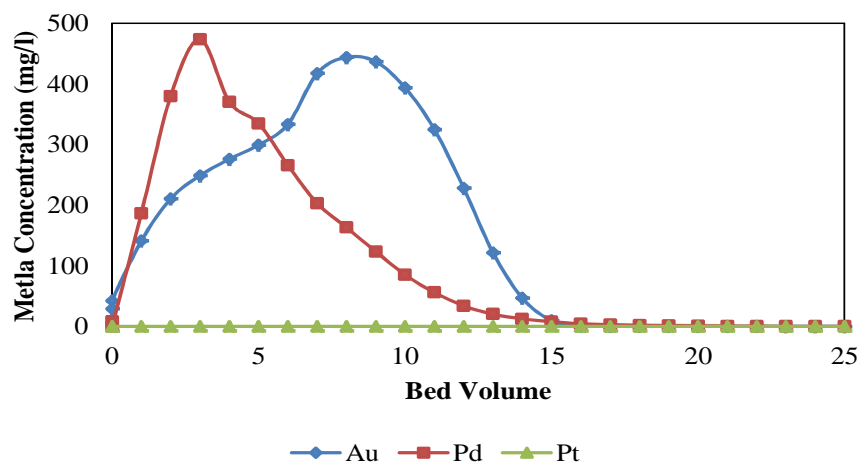
The elution conditions used for each eluant during the experimentation are presented in Table 6.2.

**Table 6.2:** Elution conditions

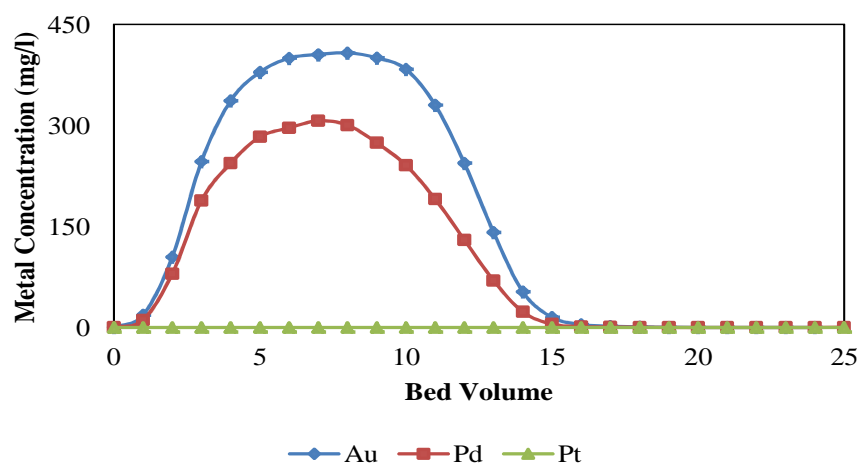
Eluting Agent	Concentration (M)	Temperature (°C)	pH	Flow (BV/h)
Acidic thiourea	0.5 Thiourea, 0.1 HCl	60	-	10.
Potassium thiocyanate	2.	22	12.0	10.
Zinc Cyanide	0.5	50	10.5	10.

Figure 6.1 shows the eluate concentration profiles of (a) Minix and (b) Amberlite PWA-5 for elution with acidic thiourea. For Minix, it can be seen that peak concentrations of palladium and gold in the eluate were low (475 ppm and 450 ppm respectively) and both peaks appeared broadly over the elution spectrum investigated. The peak concentration of palladium appeared first followed by the peak concentration of gold. No palladium and gold were present in the eluate after 15 bed volumes of acidic thiourea had passed through the bed. Acidic thiourea was unable to elute platinum from Minix at the conditions investigated, as can be observed from Figure 6.1 (a).

It can be observed from Figure 6.1 (b) that during the elution of Amberlite PWA-5 with acidic thiourea, both palladium and gold peaked after approximately five bed volumes of acidic thiourea, reaching concentrations of 400 ppm and 300 ppm respectively, in the eluate. The eluate concentration profiles of both palladium and gold from Amberlite PWA-5 appeared broadly over the elution spectrum investigated. Again no palladium and gold were present in the eluate after 15 bed volumes of acidic thiourea passed through the bed. Acidic thiourea, as with Minix, was unable to elute any of the platinum from Amberlite PWA-5. It can be seen from Figure 6.2 (a), which presents the elution profiles for Minix with acidic thiourea, that the palladium elution initially occurs faster than the gold elution. However, the elution of both these metals were complete after 15 bed volumes of acidic thiourea had passed through the bed, at which point 99% of the palladium and all of the gold was eluted from the resin. The elution profiles of palladium and gold from Amberlite PWA-5 using acidic thiourea, in Figure 6.2 (b), are very similar. The elution of both these metals was complete after 15 bed volumes of acidic thiourea had passed



(a)



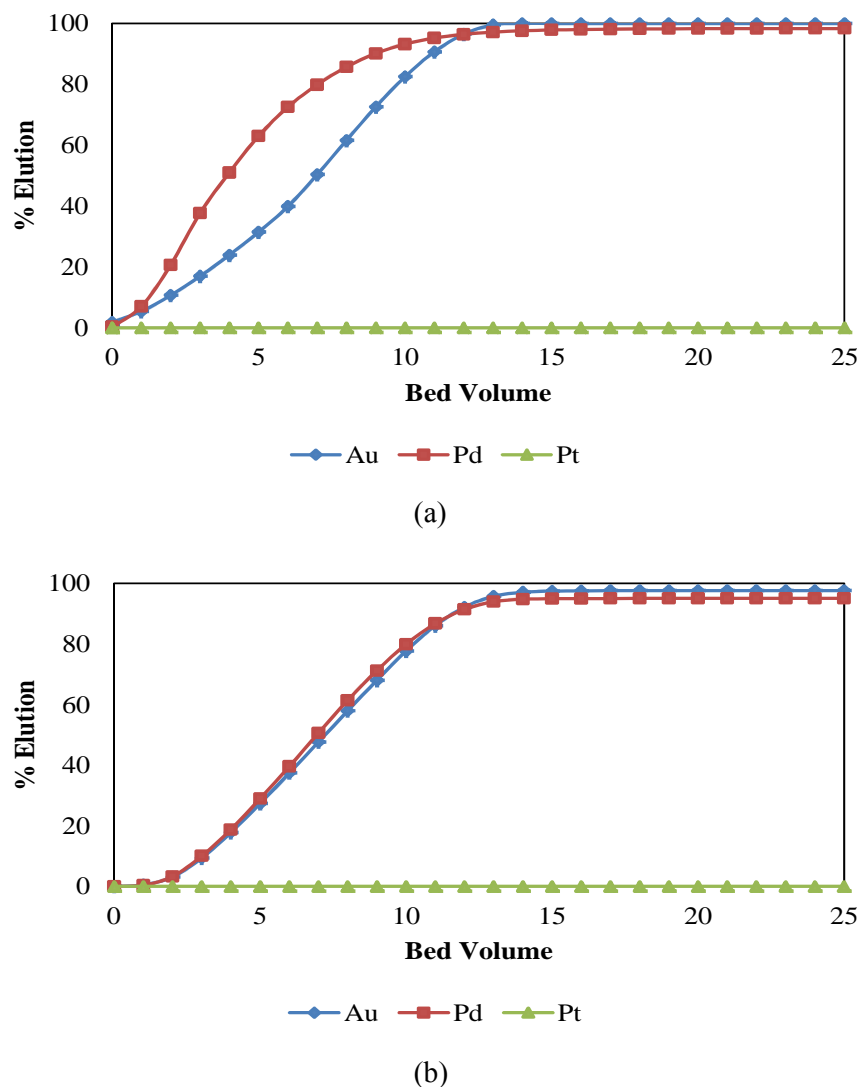
(b)

**Figure 6.1:** Eluate concentration profiles for (a) Minix and (b) Amberlite PWA-5, using acidic thiourea

through the bed, at which point 95% of the palladium and 97% of the gold was eluted from Amberlite PWA-5.

It will be observed that in the following elution method when thiocyanate was used, that thiocyanate was able to elute platinum from both Minix and Amberlite PWA-5. It was thus decided to elute Minix and Amberlite PWA-5, previously eluted with acidic thiourea, with thiocyanate, to observe if the platinum was eluted. After 2 hours of elution with 2M thiocyanate, at a flow rate of 10 BV/h, 60 % and 95% of the platinum were eluted from Minix and Amberlite PWA-5, respectively. This indicated that no transformation of the  $Pt(CN)_4^{2-}$  complex or precipitation of platinum occurred, and that the anion was still adsorbed onto the respective resins.

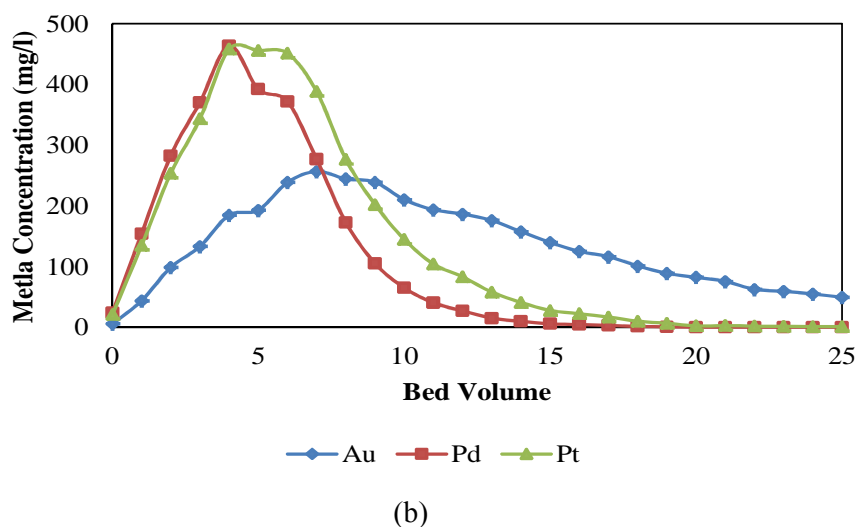
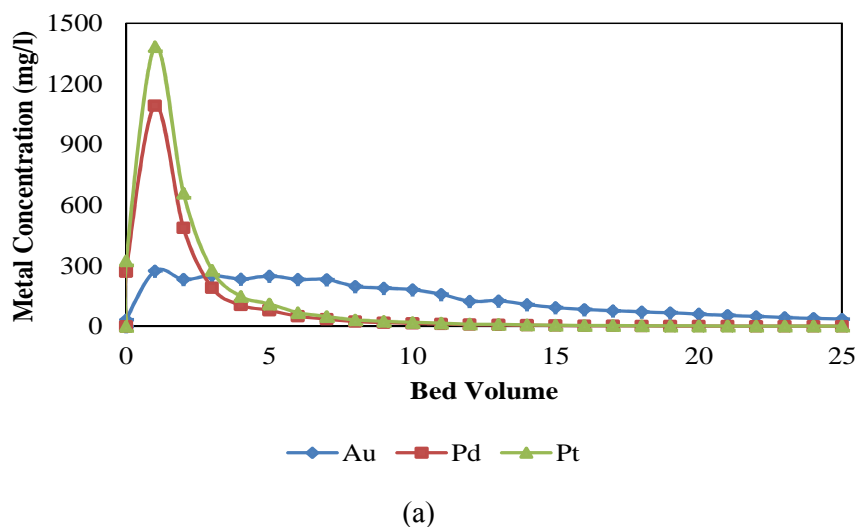
Figure 6.3 represents the eluate concentration profiles of (a) Minix and (b) Amberlite PWA-5 for elution with potassium thiocyanate. From Figure 6.3 (a) it can be seen



**Figure 6.2:** Elution profiles for (a) Minix and (b) Amberlite PWA-5, using acidic thiourea

that high peak concentrations of platinum (1400 ppm) and palladium (1050 ppm) were achieved, with a low peak concentration for gold (300 ppm) for the elution of Minix with thiocyanate. Platinum and palladium concentrations in the eluate peaked rapidly, with no tailing effect of the curve, and no more platinum and palladium were present in the eluate after nine bed volumes of thiocyanate had passed through the bed. The gold eluate concentration peaked slowly, and was followed by a long tail of the curve, with gold still being present in the eluate after 25 bed volumes of thiocyanate had passed through the column.

From Figure 6.3 (b), it can be seen that the peak concentrations of platinum (475 ppm) and palladium (475 ppm) in the eluate from Amberlite PWA-5, were lower than those for Minix, with gold (250 ppm) having a similar peak concentration. The concentration of platinum and palladium also peaked more slowly for Amberlite PWA-5, having longer



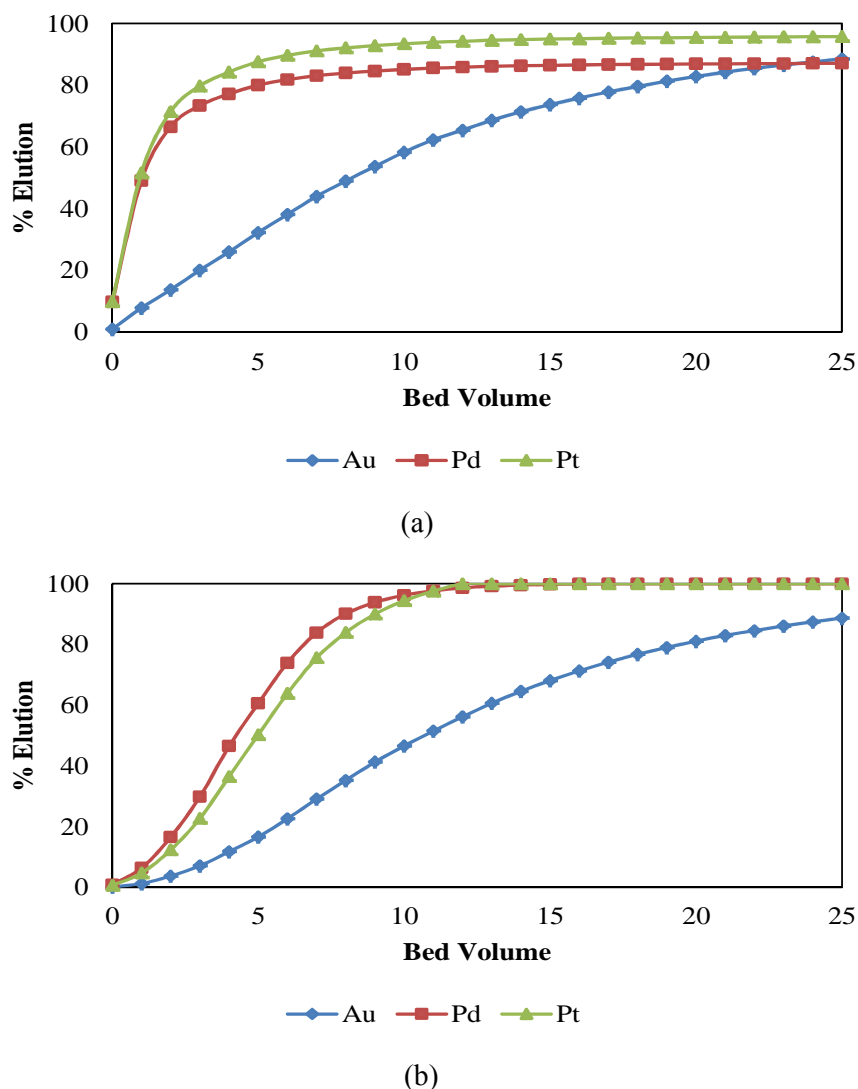
**Figure 6.3:** Eluate concentration profiles for (a) Minix and (b) Amberlite PWA-5, using potassium thiocyanate

tails for both metals. However, no palladium and platinum were present in the eluate after respectively 18 and 20 bed volumes of potassium thiocyanate had passed through the bed. A long tail for gold was present, with gold still being present in the eluate after 25 bed volumes of potassium thiocyanate had passed through the bed.

From Figure 6.4 (a), it is clear that platinum and palladium elution from Minix took place faster than the gold elution. The elution of platinum was complete after 15 bed volumes, with 95 % of the platinum eluted. Palladium elution was complete after 20 bed volumes with 88% of the palladium eluted. Gold elution did not reach completion, with 89% of the gold eluted after 25 bed volumes of potassium thiocyanate had passed through the bed.

From Figure 6.4 (b), it can be seen that the elution profiles of platinum and palladium from Amberlite PWA-5 were similar and that the elution of these metals took place





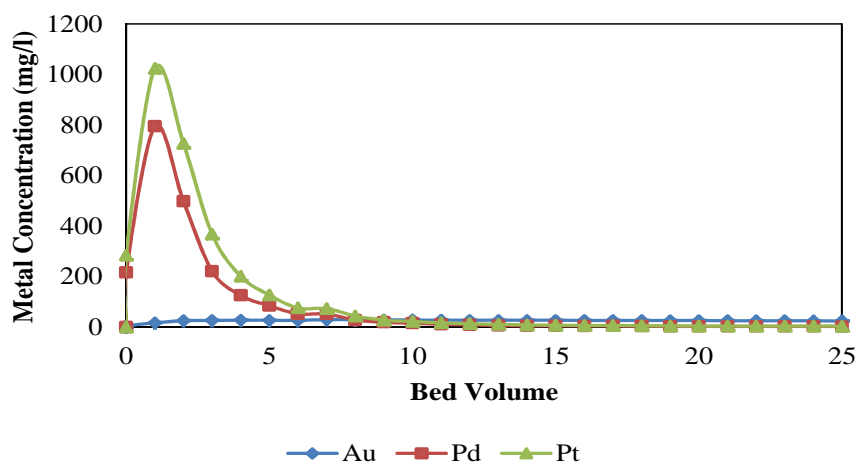
**Figure 6.4:** Elution profiles for (a) Minix and (b) Amberlite PWA-5, using potassium thiocyanate

much faster than the gold elution. Both platinum and palladium were fully eluted from Amberlite PWA-5 after 15 bed volumes of potassium thiocyanate had passed through the bed. Gold elution did not reach completion, with 89% of the gold eluted from Amberlite PWA-5 after 25 bed volumes of potassium thiocyanate had passed through the bed.

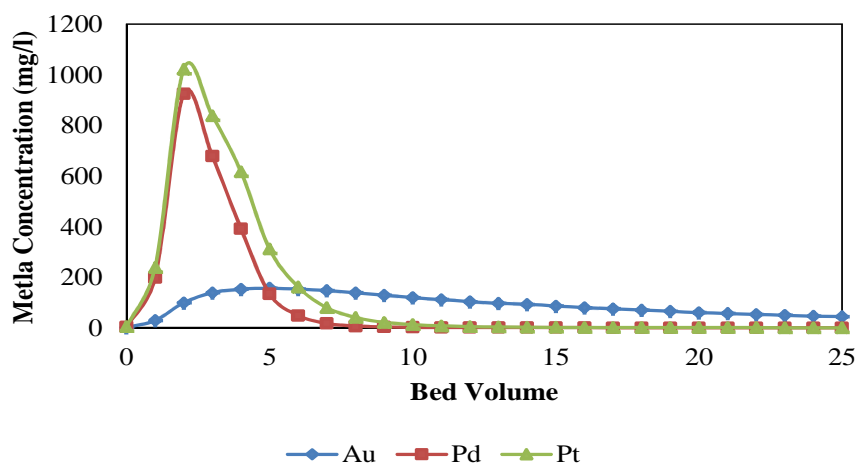
Figure 6.5, shows the eluate concentration profiles of (a) Minix and (b) Amberlite PWA-5, eluted with zinc cyanide. From Figure 6.5 (a), high eluate concentration peaks for platinum (800 ppm) and palladium (1000 ppm) can be observed, with gold having a very low eluate concentration peak of 50 ppm. The eluate concentration peaks of platinum and palladium were reached rapidly, and after 10 bed volumes of zinc cyanide had passed through the bed, no platinum or palladium was present in the eluate. Very poor elution of gold from Minix with zinc cyanide was observed, with gold having a low eluate concentration peak and long elution tail, and gold was still present in the eluate

after 25 bed volumes of zinc cyanide had passed through the bed.

From Figure 6.5 (b), sharp peaks can again be observed for the elution of platinum and palladium from Amberlite PWA-5. High concentrations of 1020 ppm for platinum and 890 ppm for palladium were reached in the eluate. No platinum or palladium were present in the eluate after 10 bed volumes of zinc cyanide had passed through the bed. The concentration profile of gold in the eluate was again broad for Amberlite PWA-5, with the gold concentration reaching a maximum of only 180 ppm, and gold still present in the eluate after 25 bed volumes of zinc cyanide had passed through the bed.



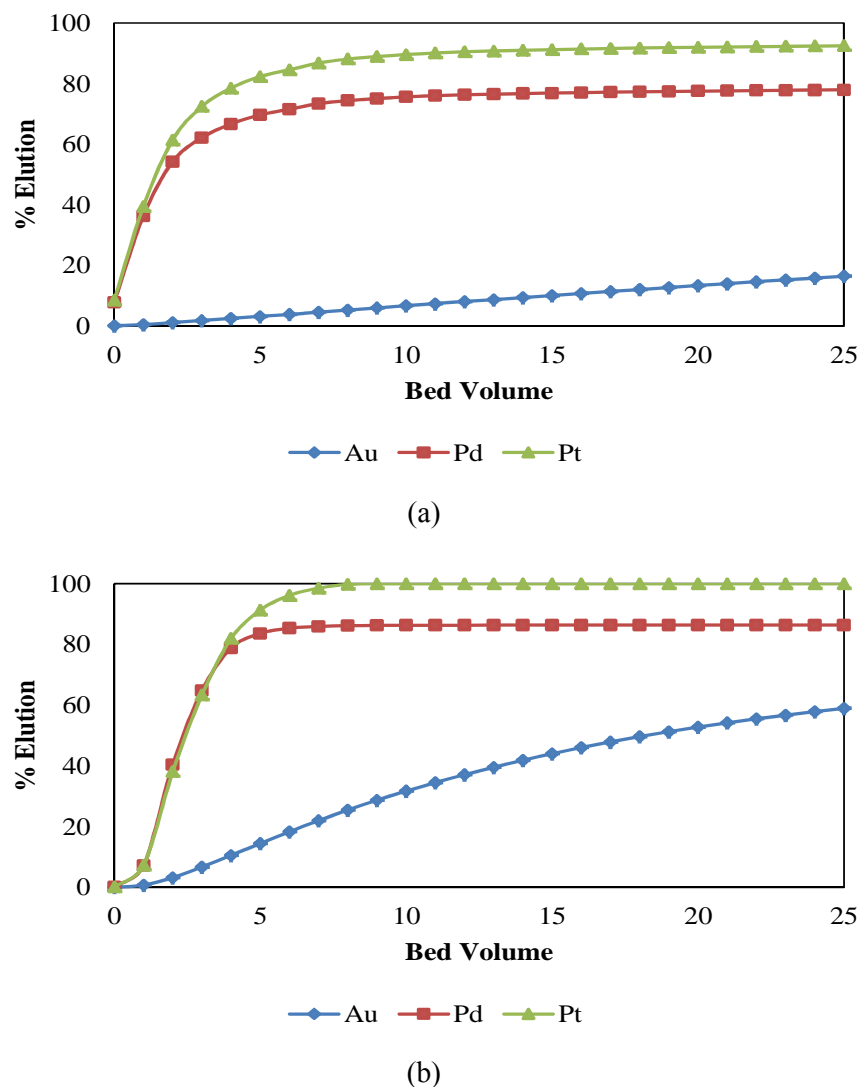
(a)



(b)

**Figure 6.5:** Eluate concentration profiles for (a) Minix and (b) Amberlite PWA-5, using zinc cyanide

Figure 6.6 shows the elution profiles of (a) Minix and (b) Amberlite PWA-5 eluted with zinc cyanide. From Figure 6.6 (a), it can be seen that platinum elution was the fastest, followed by palladium and lastly gold. Palladium and platinum elution was complete after



**Figure 6.6:** Elution profiles for (a) Minix and (b) Amberlite PWA-5, using zinc cyanide

approximately 15 bed volumes of zinc cyanide had passed through the bed after which 92% of the platinum and 79% of the palladium were eluted from Minix. Gold elution did not reach completion, and only 18% of the gold was eluted from Minix after 25 bed volumes of zinc cyanide had passed through the bed.

From Figure 6.6 (b) it can be seen that similar elution profiles for platinum and palladium were achieved, with much slower elution of gold. Platinum and palladium elution was complete after 7 bed volumes of zinc cyanide had passed through the bed, at which time 100% of platinum and 85% of palladium were eluted from Amberlite PWA-5. Gold elution did not reach completion, and only 60% of the gold was eluted from Amberlite PWA-5 after 25 bed volumes of zinc cyanide had passed through the bed.

## 6.2 The Effect of different parameters on elution

In this section the effect of different parameters, such as eluant concentration, temperature and flow rate, on the elution efficiency of the three eluants was investigated. The elution efficiency for all the experiments was defined as the percentage of each metal eluted after 15 bed volumes of the respective eluting agents had passed through the bed, as shown in Equation (6.2.1):

$$\text{Elution Efficiency}(\%) = \frac{\text{Amount of Metal Eluted after 15 Bed Volumes}(mg)}{\text{Total Loading of Metal on Resin}} \quad (6.2.1)$$

Fifteen bed volumes of eluting agent were deemed to be sufficient to observe the effect of different parameters on efficiency of the three different eluants. The investigation was performed by using the same elution conditions used in Section 6.1 for the three eluting agents, changing only one of the parameters at a time and keeping the others constant. In this section, only the elution of platinum, palladium and gold from Amberlite PWA-5 was considered, due to the excessive amount of information available on the elution from Minix, and also because Amberlite PWA-5 showed better platinum and palladium adsorption potential during the adsorption experiments.

### 6.2.1 Elution with Acidic Thiourea

The effects of changes in both the hydrochloric acid and thiourea concentration on the elution efficiency of platinum, palladium and gold are presented in Table 6.3. The hydrochloric acid concentration was increased between 0.1 M and 0.5 M in increments of 0.1 M, and the thiourea concentration was decreased from 0.7 M to 0.1 M in decrements of 0.2 M.

It can be seen, from Table 6.3 that the effect of the hydrochloric acid concentration on the elution of both gold and palladium was minimal. Slight increases in the elution of both metals can be observed as the hydrochloric acid concentration was increased from 0.1 M to 0.2 M. Above 0.2 M hydrochloric acid in solution, all of the palladium and gold could be eluted from Amberlite PWA-5, within 15 bed volumes. Platinum elution, however, still did not occur, even when the hydrochloric acid concentration was increased to 0.5 M.

The effect of thiourea concentrations on the elution of palladium and gold, however, was more noticeable than was observed for the hydrochloric acid concentration. With 0.1 M of thiourea solution, only 32% of the gold and 25% of the palladium were eluted from the resins, within 15 bed volumes. When the thiourea concentration was increased to 0.3 M, a significant increase in the elution efficiency of both gold and palladium, to 97% and

**Table 6.3:** Effect of different parameters on elution efficiency with acidic thiourea

Effect of HCl Concentration (Thiourea, 0.5M; Temperature, 60°C; Flow rate, 10 BV/h)				
HCl, (M)	Au	Pd	Pt	
0.1	97	95	0	
0.2	101	100	0	
0.3	100	100	0	
0.4	100	100	0	
0.5	100	100	0	
Effect of Thiourea Concentration (HCl, 0.1M; Temperature, 60 °C; Flow rate, 10 BV/h)				
Thiourea, (M)	Au	Pd	Pt	
0.1	32	25	0	
0.3	97	94	0	
0.5	97	95	0	
0.7	100	100	0	

94% respectively, was achieved. However, when the thiourea concentration was increased above 0.3 M, no significant increase in the elution efficiencies of gold and palladium was observed, with all of the palladium and gold eluted from Amberlite PWA-5 with the use of 0.7 M thiourea. No platinum elution was achieved over the entire thiourea concentration range investigated.

Monlien *et al.* (2002), found that  $Pd(CN)_4^{2-}$  becomes 400 times more reactive than  $Pt(CN)_4^{2-}$  in low pH solutions, because of the formation of  $[Pd(CN)^3HCN]^-$ . Thus this can explain the ineffective elution of platinum with the use of acidic thiourea, even at different hydrochloric acid and thiourea concentrations. A possible kinetic effect is imposed on the reaction between thiourea and  $Pt(CN)_4^{2-}$  during the elution. This is caused by the low pH of the solution, causing the ineffective elution of platinum cyanide.

### 6.2.2 Elution with Potassium Thiocyanate

The effects on the elution of platinum, palladium and gold during changes in concentration, temperature and flow rate of potassium thiocyanate are shown in Table 6.4. The potassium thiocyanate concentration was varied between 0.5 M and 2 M, the temperature between 22°C and 50°C and the flow rate between 5 BV/h and 20 BV/h.

It can be seen from Table 6.4 that the concentration of potassium thiocyanate had a significant effect on the elution of gold platinum and palladium, below a concentration of 1 M. At a concentration of 0.5 M, only 29% of gold, 49% of palladium and 35% of platinum

**Table 6.4:** Effect of different parameters on elution efficiency with potassium thiocyanate

<b>Effect of Thiocyanate Concentration</b> (Temperature, 22 °C; Flow rate, 10 BV/h)			
<b>Thiocyanate, (M)</b>	<b>Au</b>	<b>Pd</b>	<b>Pt</b>
0.5	29	49	35
1	66	100	94
1.5	68	100	94
2	68	100	100
<b>Effect of Temperature</b> (Thiocyanate, 2M; Flow rate, 10 BV/h)			
<b>Temperature, (°C)</b>	<b>Au</b>	<b>Pd</b>	<b>Pt</b>
22	68	100	100
30	65	92	97
40	69	89	91
50	70	85	90
<b>Effect of Flowrate</b> (Thiocyanate, 2M; Temperature, 22°C)			
<b>Flow rate, (BV/h)</b>	<b>Au</b>	<b>Pd</b>	<b>Pt</b>
5	72	97	96
10	68	100	100
15	57	91	99
20	61	96	94

were eluted from Amberlite PWA-5 within 15 bed volumes. When the concentration of potassium thiocyanate was increased to 1 M, the elution efficiency of the metals increased to 66% for gold, 100% for palladium and 94% for platinum. However, a further increase in potassium thiocyanate concentration to 2 M, resulted in only a slight increase in the elution of gold and platinum, to 68% and 100% respectively.

The effect of temperature on the elution efficiency was small for all three metals. However a difference in the effect of temperature on the elution of gold and the elution of platinum and palladium was noticed. The elution efficiency of gold increased from 68% to 70%, whereas the elution efficiency of palladium and platinum decreased from 100% to 85% and from 100% to 90% respectively, as the temperature was raised from 22°C to 50°C. It is unclear why this happened, and could be that at a high temperature the resin prefers the metal cyanide anions of palladium and platinum, to the thiocyanate anion.

The elution flow rate of potassium thiocyanate had a larger effect on the elution of gold, than on the elution of palladium and platinum. At a flow rate of 5 BV/h, 72% of the gold was eluted within 15 bed volumes, however, as the flow rate was increased to 20 BV/h, only 61% of the gold was eluted within 15 bed volumes. No general trend on the

elution efficiency of palladium and platinum could be observed, however, over the entire flow rate range investigations more than 90% of both metals was always eluted within 15 bed volumes.

### 6.2.3 Elution with Zinc Cyanide

The effect of changes in zinc cyanide concentration, temperature and flow rate on the elution of gold, palladium and platinum, is presented in Table 6.5. The zinc cyanide concentration was varied between 0.15 M and 1 M, the temperature between 30°C and 60°C and the flow rate between 5 BV/h and 20 BV/h.

**Table 6.5:** Effect of different parameters on elution efficiency with zinc cyanide

<b>Effect of Zinc Cyanide Concentration</b> (Temperature, 50 °C; Flow rate, 10 BV/h)			
<b>Zinc Cyanide, (M)</b>	<b>Au</b>	<b>Pd</b>	<b>Pt</b>
0.15	33	94	88
0.3	46	100	99
0.5	42	86	90
0.75	60	96	90
1	64	96	90
<b>Effect of Temperature</b> (Zinc Cyanide, 0.5M; Flow rate, 10 BV/h)			
<b>Temperature, (°C)</b>	<b>Au</b>	<b>Pd</b>	<b>Pt</b>
30	43	93	90
40	48	87	86
50	42	86	90
60	53	84	84
<b>Effect of Flowrate</b> (Zinc Cyanide, 0.5M; Temperature, 50°C)			
<b>Flow rate, (BV/h)</b>	<b>Au</b>	<b>Pd</b>	<b>Pt</b>
5	55	99	97
10	42	86	90
15	43	95	94
20	42	95	95

The effect of zinc cyanide concentration was more severe on the elution of gold than on the elution of platinum and palladium. The gold elution efficiency increased from 33% to 64% as the zinc cyanide concentration was increased from 0.15 M to 1 M. However no significant change in the gold elution efficiency between 0.3 M and 0.5 M and again between 0.75 M and 1 M, was observed. No clear trend for the effect of zinc cyanide

concentration on the elution efficiencies of platinum and palladium was observed in the zinc cyanide concentration range investigated, and in most of the cases more than 90% of both platinum or palladium was eluted from the resin, within 15 bed volumes.

Temperature did not have a large effect on the elution of any of the three metals. Gold elution increased from 43% to 53% as the temperature was increased from 30°C to 60°C. Again, as with the potassium thiocyanate elution, the elution efficiencies of both palladium and platinum decreased slightly as the temperature of the eluting agent was increased from 30°C to 60°C. This indicates that temperature has a definite effect on displacement mechanism involved, when the anions,  $Pt(CN)_4^{2-}$  and  $Pt(CN)_4^{2-}$ , are displaced from the resin by either  $SCN^-$  or  $Zn(CN)_4^{2-}$  anions.

The elution efficiencies of all three metals was definitely better at the lowest flow rate of 5 BV/h, with the elution of 55% of gold, 99% of palladium and 97% of platinum. However, as the flow rate was increased to 10 BV/h and higher, no significant change in the elution efficiency of any of the metals was observed, with gold elution ranging between 42% and 43%, palladium elution between 86% and 95% and platinum elution between 90% and 95%.

### 6.3 Combined Base Metal Elution

During this experiment Amberlite PWA-5 was loaded with solution containing 10 ppm of each of the metals, platinum, palladium, gold, zinc, nickel, copper and iron, with a free cyanide concentration of 150ppm and pH 10.5. The resin was contacted with the solution in rolling bottles for 48 hours, after which it was separated from the solution, by filtration. Samples were taken from the solution before and after the experiment for ICP-OES analysis, and the loading on the resin determined by mass balance. The average metal loadings on the resin for the experiment are shown in Table 6.6.

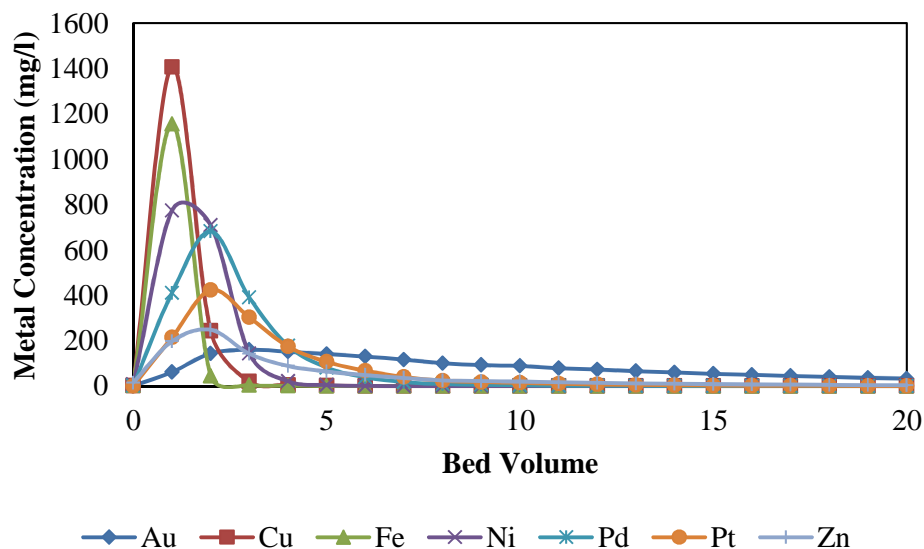
**Table 6.6:** Loading of metals for combined base metal elution

Metal Loading (mg/l)						
Au	Pt	Pd	Zn	Ni	Cu	Fe
2078	1820	1884	1210	1698	1920	1240

Five millilitres of wet settled loaded resin were introduced into the elution columns for each experiment. In previous elution sections, the ineffective elution of platinum with acidic thiourea was emphasized, and thus acidic thiourea was not considered for this experiment. The conditions used for the thiocyanate elution were a 2M thiocyanate solution containing 150 ppm free cyanide at pH 12 and a temperature of 22°C, and for zinc



cyanide, the elution conditions used were 0.5M zinc cyanide at pH 10.5 and a temperature of 50°C. Both elutions were performed at a flow rate of 10 BV/h, collecting samples of each bed volume of eluate coming through the column, for a period of 20 bed volumes. From the results of the samples, eluate concentration and elution profiles could be generated for both elution methods.



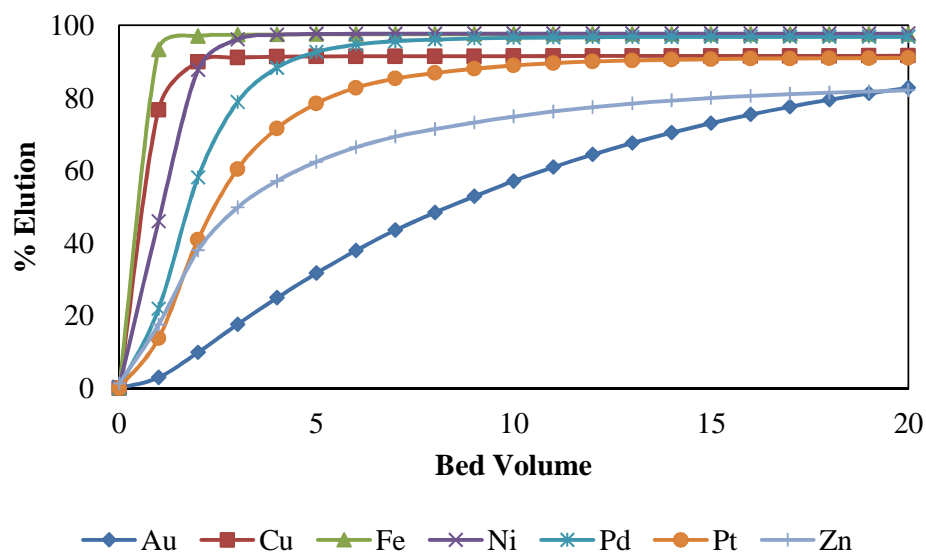
**Figure 6.7:** Eluate concentration profile for Amberlite PWA-5 loaded with multiple metals, using potassium thiocyanate

Presented in Figure 6.7 is the eluate concentration profile for the elution of Amberlite PWA-5, using potassium thiocyanate. It can be seen from Figure 6.7, based on the peak concentration of each metal, that metals were eluted from the resin in the following decreasing sequence: copper > iron > nickel > zinc > palladium > platinum > gold. The concentration peaks of both copper and iron are sharp, with no tailing of the eluate concentration curves. After three bed volumes of potassium thiocyanate had passed through the column, it can be seen that the concentrations of copper and iron in the eluate are approximately zero.

The rapid elution of iron and copper from the resin with the use of potassium thiocyanate can be attributed to the charge of each of these metal cyanide complexes. The tri-ethyl functionality of Amberlite PWA-5, is unable to associate closely with these highly charged anions, and thus they are easily displaced from the resin by the mono-valent thiocyanate anion, for which the resin has a higher affinity.

The eluate concentration peaks for the cyanide complexes of nickel, palladium, platinum and zinc are broader, and only occur after most of the copper and iron has been

removed from the resin. All four of these cyanide complexes are divalent in nature, and thus it was expected that they would bind more strongly to the resin than the cyanide complexes of iron and copper, and thus be eluted with more difficulty. The eluate concentration profile for gold exhibited a broad peak with a long tail. Thus of all the metals, gold was the most difficult to remove with the use of potassium thiocyanate.

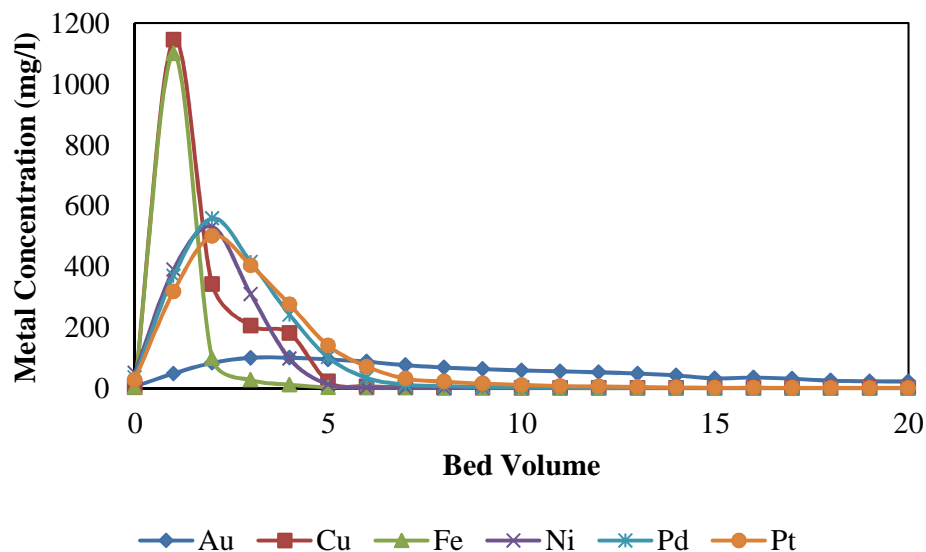


**Figure 6.8:** Elution profile for Amberlite PWA-5 loaded with multiple metals, using potassium thiocyanate

Presented in Figure 6.8 is the elution profile of Amberlite PWA-5 eluted with potassium thiocyanate. From Figure 6.8 it can be seen that copper and iron were rapidly removed from the resin, followed by nickel, palladium and platinum. The elution of both zinc and gold was slow, reaching approximately 80% elution after 20 bed volumes of potassium thiocyanate had passed through the column. All other metals present could be eluted to more than 90% within 20 bed volumes.

Although all metals were eluted to a sufficient extent from the resin, no indication of a split elution of metals could be observed with potassium thiocyanate. The elution of copper and iron was very fast, but not fast enough to be separated from nickel, palladium and platinum. The slow elution of gold from the resin with potassium thiocyanate can be investigated as an alternative for separating gold from the other metals present on the resin.

Presented in Figure 6.9 is the eluate concentration profile for Amberlite PWA-5, using zinc cyanide. It is shown in Figure 6.9 that based on the peak concentration of each metal, the metals were eluted in the following decreasing sequence: copper > iron >

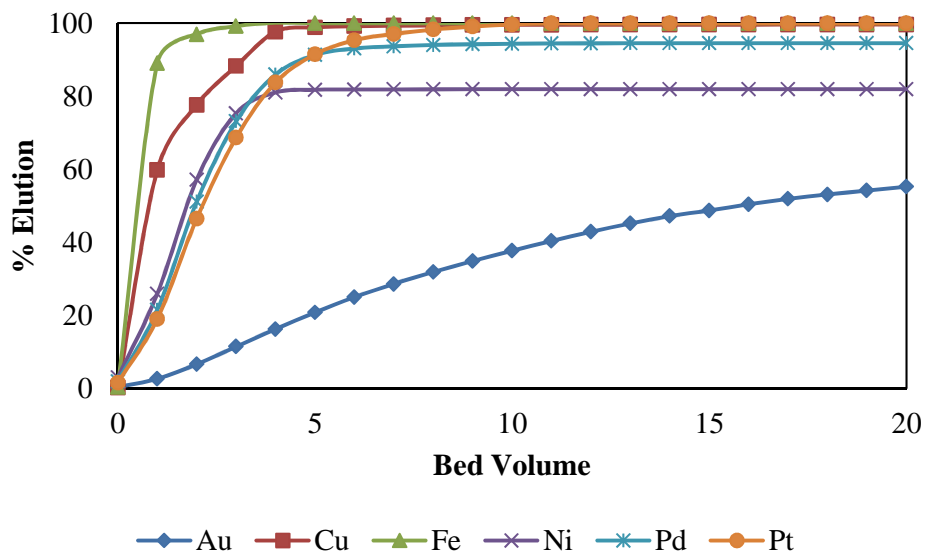


**Figure 6.9:** Eluate concentration profile for Amberlite PWA-5 loaded with multiple metals, using zinc cyanide

nickel > platinum > palladium > gold. The elution sequence is very similar to that previously observed for the potassium thiocyanate elution. Zinc was not included in the eluate concentration profile, because zinc cyanide was used to elute the resin. The peak concentrations of both copper and iron are sharp with no tailing of the curve. No copper and iron were present in the eluate after four bed volumes of zinc cyanide had passed through the bed. Again the rapid elution of these two metals is a result of the low affinity that Amberlite PWA-5 has for highly charged anions, and thus would rather load the divalent zinc cyanide anion.

The eluate concentration profiles of nickel, platinum and palladium were broader, indicating that the zinc cyanide anion found it more difficult to displace them from the resin. The concentration peaks of these three metals also only occurred after most of the iron and copper was displaced from the resin. These metal cyanide complexes are divalent in nature and thus are more strongly adsorbed by the resin. After six bed volumes of zinc cyanide had passed through the bed, no nickel was present in the eluate, and only after approximately nine bed volumes, no more platinum and palladium were present in the eluate. The eluate concentration profile of gold had a gradual peak and a long tail, indicating that gold was the most difficult to displace of all the metals, when using zinc cyanide. The monovalent nature of the aurocyanide complex, resulted in the anion being strongly adsorbed by the resin, making physical elution very difficult.

Presented in Figure 6.10 is the elution profile for Amberlite PWA-5, using zinc cyanide. From Figure 6.10 it can be seen that complete elution of copper, iron and platinum



**Figure 6.10:** Elution profile for Amberlite PWA-5 loaded with multiple metals, using zinc cyanide

was possible with zinc cyanide, with more than 90% of palladium eluted, within 20 bed volumes. Effective elution of more than 80% for nickel was achieved with zinc cyanide. Gold elution progressed much more slowly than all other metals present on the resin, and a final elution efficiency of just under 60% was achieved, within 20 bed volumes.

Again as with potassium thiocyanate elution, no indication for selectively separating the different metals during elution was observed. Copper and iron elution progressed too slowly for their separation from the other metals to be considered. Gold elution, however, was sufficiently slow to make it desirable to consider an alternative elution method.

## Chapter 7

# Conceptual Flow Sheet Development

### 7.1 Flow Sheet Generation

Based on the findings of all the experimental work and information found during the literature study, some flow sheet options for the recovery of platinum, palladium and gold from the pregnant cyanide solution are discussed here. Figure 7.1 shows the most basic process flow diagram possible for the recovery of platinum, palladium and gold from cyanide solutions, using ion exchange resins. The process flow diagram consists of an adsorption stage, an elution stage, a regeneration stage and a metal recovery stage. The purpose of the process flow diagrams is to produce a product stream that contains platinum, palladium and gold extracted from the leach which can be sent directly to a precious metal refinery (PMR).

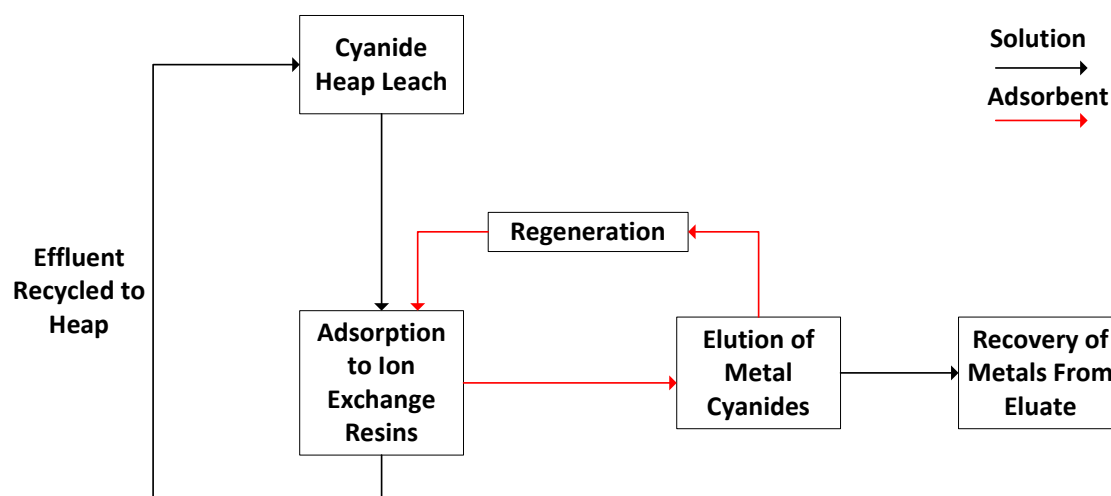


Figure 7.1: Basic flow diagram for ion exchange process

At the completion of the project, two conceptual flow diagrams were generated. During experimentation, Minix and Amberlite PWA-5 were found to have the greatest platinum

cyanide, palladium cyanide and aurocyanide adsorption potentials. Minix was shown to have a higher affinity for the aurocyanide complex than for all the other metal cyanide complexes in the pregnant heap leach solution. The strong base anion exchange resin, Amberlite PWA-5 could recover platinum cyanide, palladium cyanide and aurocyanide from the solution, with minimal adsorption of iron cyanide.

Figure 7.2 shows the first conceptual flow diagram. The process begins with the pregnant cyanide leach solution going to an adsorption stage that contain Amberlite PWA-5. From the adsorption results it was seen that Amberlite PWA-5 could, with repeated contacts, effectively extract platinum cyanide, palladium cyanide and aurocyanide from the PLS, with lower extractions of the base metal cyanides of copper and iron. The effluent from the heap leach is then recycled to the heap, to eliminate the loss of valuable metals still present in the solution.

The loaded Amberlite PWA-5 is then sent to the elution section where it is eluted with zinc cyanide. Although potassium thiocyanate was also found to be effective in the elution of platinum cyanide, palladium cyanide and aurocyanide during the elution experiments performed in this project, this eluant has to date only been used on experimental scale because of the complex regeneration of a strong base resin eluted with thiocyanate. Acidic thiourea on the other hand, eluted platinum cyanide from Amberlite PWA-5 poorly, and thus if this eluant is used, a additional elution step will be needed to elute platinum cyanide from Amberlite PWA-5. Thus zinc cyanide was selected for this flow diagram because it effectively eluted all the metal cyanides from the resin during the elution experiments performed in this project, and because the eluant has been used on industrial scale for the elution of aurocyanide from strong base anionic resins (Fleming, 1998; Fleming and Cromberge, 1984*c*).

After the resin is eluted it is sent to a regeneration section, where the loaded zinc cyanide is removed from the resin, using either sulfuric or hydrochloric acid, prior to the resin being recycled to the adsorption section. The effluent from the regeneration section is then sent to an alkaline solution, where zinc cyanide is recovered to be re-used for elution. The eluate is then taken to a relevant recovery process to recover platinum, palladium and gold, from where this concentrated solution is sent to the precious metal refinery (PMR). The recovery options that were included here are zinc cementation, thermal hydrolysis and electrowinning.

The second flow diagram is shown in Figure 7.3. The process begins with the PLS going to an adsorption section that will only contain Minix. From the adsorption experimental work it was concluded that Minix had a higher affinity for the aurocyanide anion than for all the other metal cyanides present in the solution. Thus the goal of this process is to selectively extract the gold from the cyanide solution first.

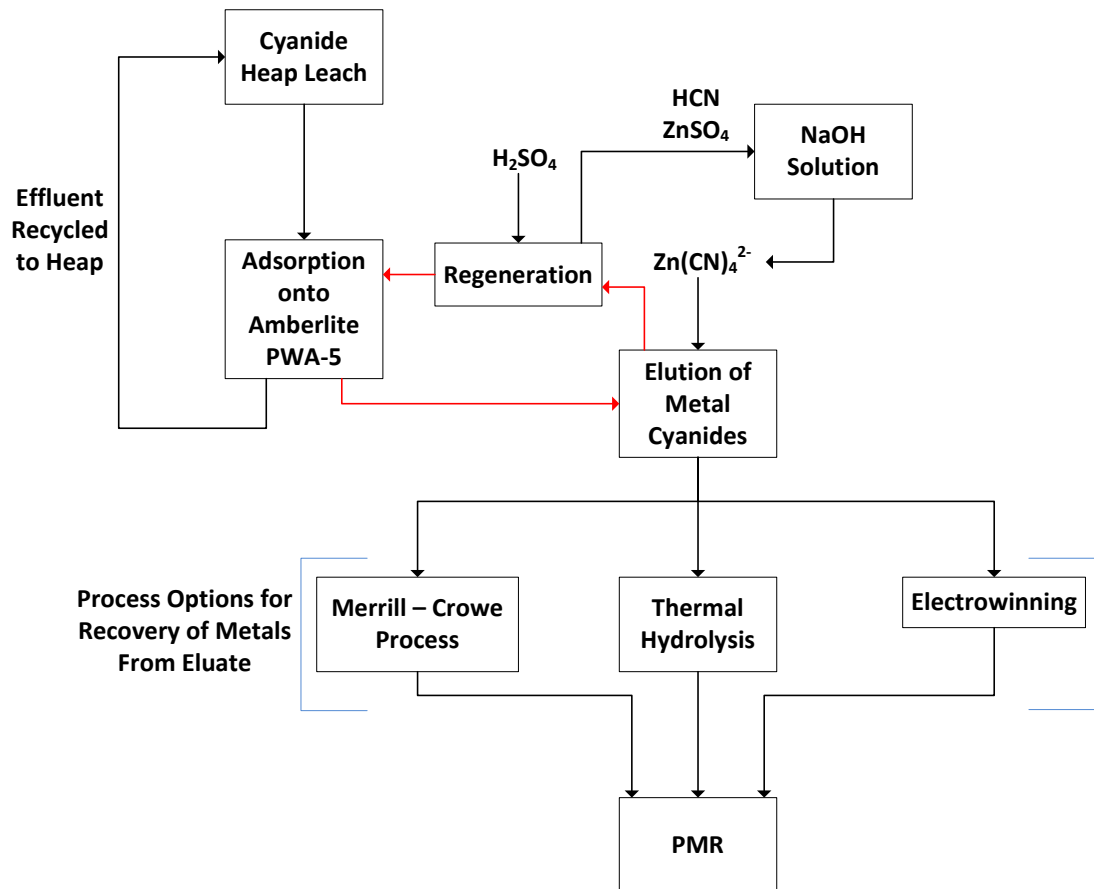


Figure 7.2: Conceptual flow diagram 1

The loaded Minix resin is then transferred to an elution section where it is eluted with acidic thiourea. The eluate from the elution section is then sent to electrowinning to recover the gold, which will then be sent to the PMR. When using acidic thiourea as eluant, no regeneration of the resin is required and thus it can be sent directly back to the adsorption section after elution. This elution-electrowinning process has been very successful, both on experimental and industrial scale (Conradie *et al.*, 1995; Fleming and Cromberge, 1984*c,a*).

The effluent from the first adsorption section will then be taken to a second adsorption section where Amberlite PWA-5 will be present for the recovery of platinum and palladium from the cyanide solution. In this section of this second flow diagram, the effluent from the first adsorption section is treated in the same manner proposed in the first flow diagram.

When comparing the two conceptual flow diagrams with each other, the following noteworthy facts emerge:

- Process 1 consists of only one adsorption and one elution stage, with the extraction of gold, platinum and palladium performed with the use of Amberlite PWA-5. Process 2 consists of a gold recovery process, using Minix and a subsequent platinum and

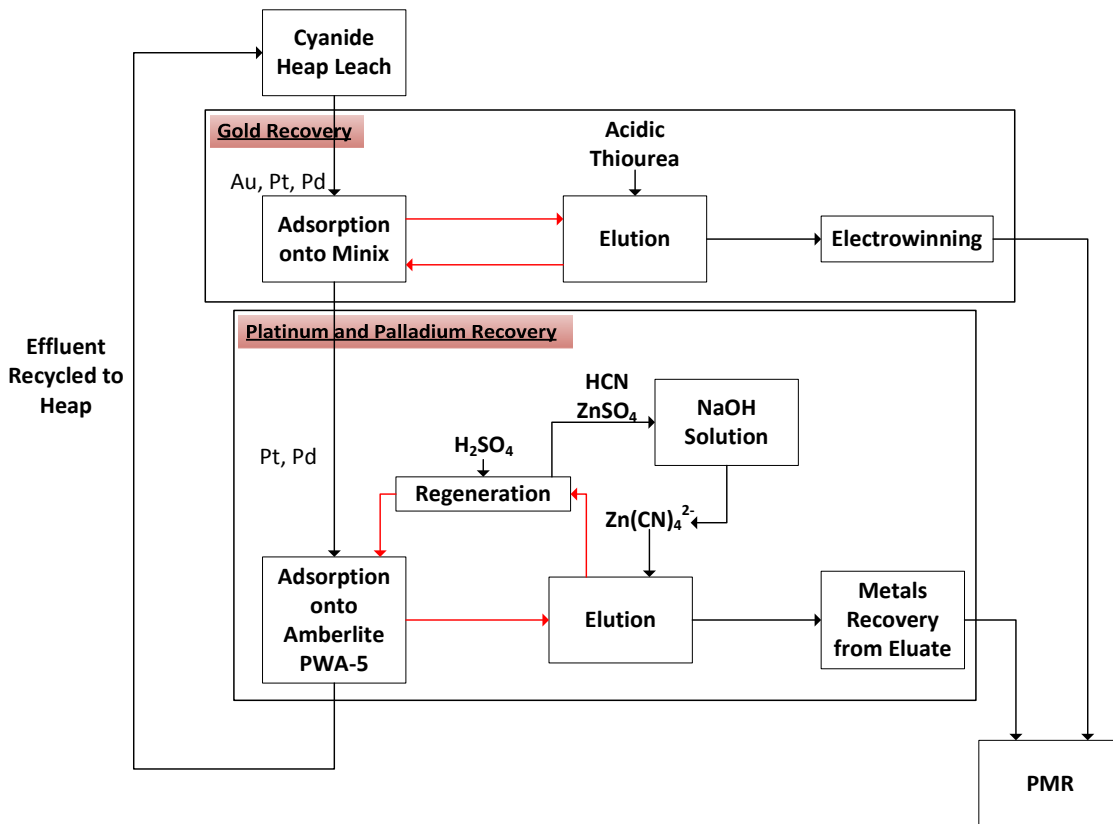


Figure 7.3: Conceptual flow diagram 2

palladium recovery process using Amberlite PWA-5, which results in two elution stages being required.

- Within the first process proposed, the subsequent recovery process needed to recover platinum and palladium from the elute is still unknown. Processes such as zinc cementation and electrowinning, although proven to be effective in the recovery of gold, studies on the recovery of platinum and palladium with these processes concluded ineffective recovery of these metals (Desmond *et al.*, 1991; Kuczynski *et al.*, 1992).
- The second process provides the means of recovering gold, platinum and palladium with processes already proven on laboratory and industrial scale. The elution of gold from Minix, with subsequent elution using acidic thiourea and electrowinning to recover gold from the eluate, is a well-known process. Platinum and palladium can then be recovered from the zinc cyanide eluate using thermal hydrolysis, which was found in studies to be an effective method for the recovery of these metals from alkaline cyanide solution (Kuczynski *et al.*, 1992; Desmond *et al.*, 1991).

When considering these two proposed processes it is seen that process 1 is more applicable for the treatment of the dilute cyanide solution. Process 1 provides a less complicated



method of recovering gold, platinum and palladium in one adsorption section, where in process 2 an additional adsorption and elution section is required. However more research is needed to make the process for the effective recovery of platinum, palladium and gold from the zinc cyanide eluate feasible.

## 7.2 Additional Flow Sheet Considerations

### 7.2.1 Pre-concentration of Pregnant Leach Solution (PLS)

From the adsorption experiments performed, it was concluded that significant improvement in both the loading and loading rate of platinum, palladium and gold onto Minix and Amberlite PWA-5 can be achieved with higher concentrations of these metals in the PLS. Thus it is proposed that a pre-concentration process be included, before the adsorption section of the process, as shown in Figure 7.4.

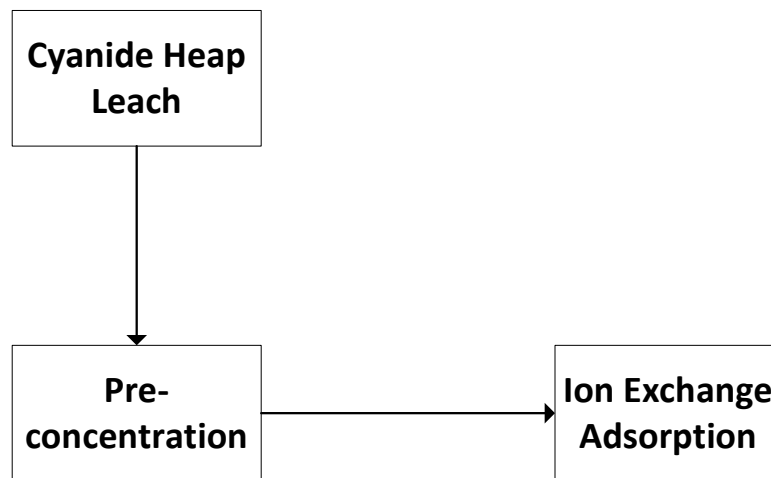


Figure 7.4: Additional pre-concentration step

The pregnant leach solution in its current state, is very dilute in platinum, palladium and gold ( $0.5\text{ppm} < \text{ppm}$ ) and contains base metals in much higher concentrations ( $> 5\text{ppm}$ ). Although there are detailed studies available on the recovery of gold from cyanide solutions, the gold concentration in these studies was never less than 1 ppm. The PLS in its present condition will result in long adsorption times and low loadings of platinum, palladium and gold on the resin.

Thus including a pre-concentration process should be considered, to increase the concentrations of platinum, palladium and gold to at least above 1 ppm. The pre-concentration step can include a process such as reverse-osmosis. Reverse-osmosis can

be used to remove most of water from the solution, thus concentrating all metal cyanide anions present in solution, prior to adsorption.

The pre-concentration step can also include a process that removes some of the base metal cyanides, such as those of copper, zinc and nickel as metal sulphites from the solution without precipitating significant amounts of platinum, palladium and gold, such as in the SART process. The SART process is derived from an acronym describing the unit operations in the process flowsheet, as follows, (1) sulphidization, (2) acidification, (3) recycling of precipitate(s) and (4) thickening of precipitate(s) (Barter *et al.*, 2001). A simplified process flow diagram of the process as used in the gold industry is shown in Figure 7.5.

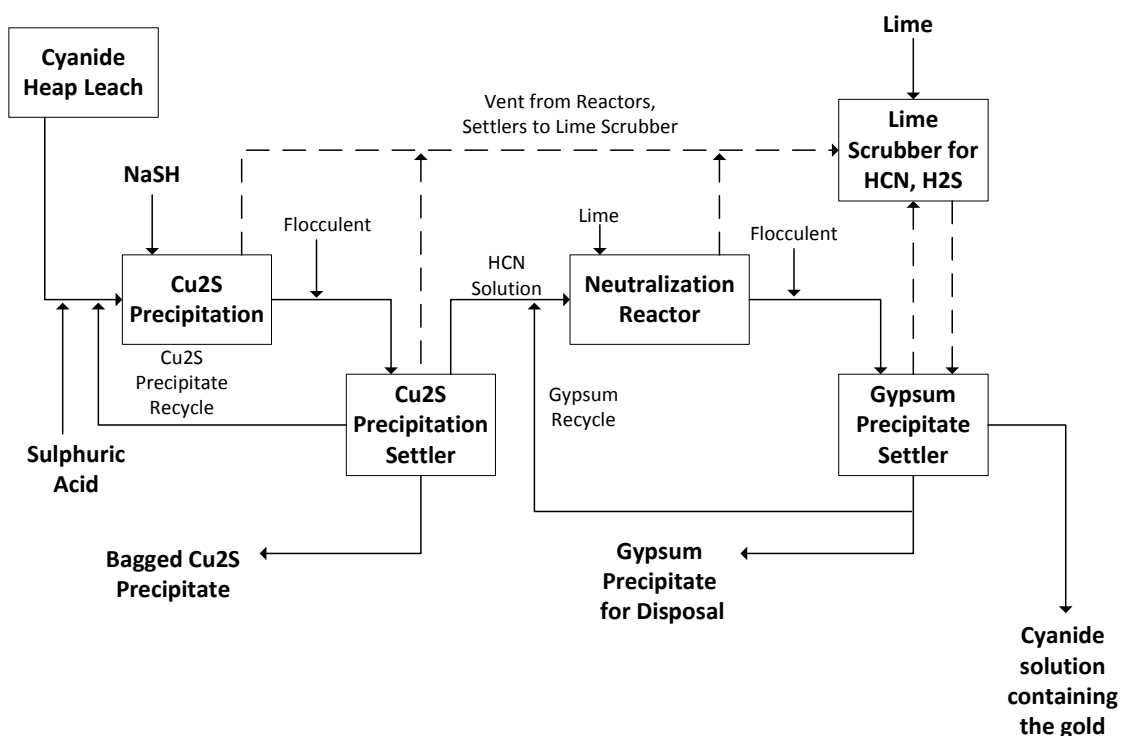


Figure 7.5: SART process

If the SART process is used to process a solution that contains significant amounts of zinc, zinc will be removed as ZnS along with copper sulphite. If this process is considered in the current ion exchange process being investigated, two process options for the use of the SART process can be used, namely:

- The SART process can be used to remove most of the copper and zinc from the pregnant cyanide leach solution prior to adsorption. This will eliminate excessive loading of copper cyanide and zinc cyanide on the resins, which in return will lead to low concentrations of copper in the eluate. Zinc cyanide will still be present in significant amounts, because zinc cyanide is the proposed eluant for the process.

Another advantage of using the SART process prior to adsorption, is that the remaining copper in solution will be present in its trivalent state, because of the high concentration of free cyanide in product stream from the SART process (Barter *et al.*, 2001). The trivalent copper cyanide anion does not load well on either Minix or Amberlite PWA-5.

- The process can also be used to treat the eluate. This solution contains high amounts of copper and especially zinc. Thus if the SART process is used, the majority of copper and zinc can be removed from the eluate solution, without removing platinum, palladium and gold from the solution.

### 7.2.2 Acid Wash Prior to Elution

In the elution experiments it was found that significant amounts of base metal cyanides were eluted along with platinum cyanide, palladium cyanide and aurocyanide, under the elution conditions used. Also, no split elution alternative was noticed in any of the experiments performed, except with the use of acidic thiourea that proved to be inadequate in the elution of platinum cyanide from the resins, although there was effective elution of palladium cyanide and aurocyanide. However, the goal of this project is to recover platinum and palladium together and not separately, and thus acidic thiourea cannot be used for this purpose.

An alternative process for the removal of some of the base metal cyanides, such as those of zinc and nickel prior to the elution of platinum cyanide, palladium cyanide and aurocyanide, is a dilute acid wash as shown in Figure 7.6.

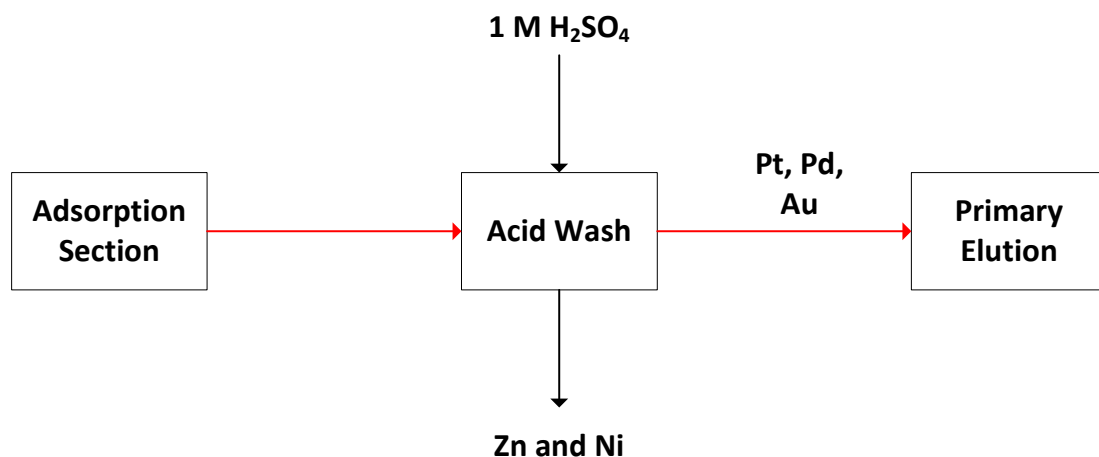


Figure 7.6: Additional acid wash step

The process works on the basis that the cyanide complexes of zinc and nickel are weak acid dissociable, compared with the cyanide complexes of platinum, palladium and gold that are strong acid dissociable. Thus when the loaded resin is treated with a dilute acid solution prior to the primary elution process, the majority of zinc and nickel loaded on the resin will be removed, making the eluate from the primary elution section purer in platinum, palladium and gold. This process is also established and has proven itself both on laboratory and commercial scale for the treatment of loaded strong base anionic resins (Conradie *et al.*, 1995).

## Chapter 8

# Conclusions and Recommendations

### 8.1 Conclusions from this Work

It can be concluded from this study that commercially available ion exchange resins can be used to effectively extract platinum, palladium and gold from cyanide heap leach solutions. Of all the resins screened in the study, strong base anionic resins showed the greatest potential for extracting these metals from cyanide solutions that contained low concentrations ( $< 1\text{ppm}$ ) of platinum, palladium and gold. However, these resins also had a tendency to co-adsorb significant amounts of base metal cyanides from the solution, especially those of zinc and nickel. Four strong base anionic resins, namely, Dowex 21K XLT, Amberjet 4600, Amberlite PWA-5 and Minix, were selected during the screening, to be investigated further. The selection of these four resins was made on their high platinum, palladium and gold recovery potentials and to compare different exchange capacities and functionalities during subsequent experimentation.

Rapid recovery of platinum, palladium and gold could be obtained with the use of strong base resins. However, as with the screening, the recoveries of base metals onto these resins were similar to those of platinum, palladium and gold, when strong base resins with high exchange capacities and smaller functionalities were used. Single component and multicomponent isotherms were generated, indicating that a significant decrease in loading of platinum, palladium and gold occurred for all resins, from a single component solution to a multicomponent solution. It was concluded that the base metals present in the multicomponent solution caused the decrease in the loading of these metals.

From the repeated loading experiments, it was concluded that the exchange capacity and functionality of the resins played an important role in their affinity for different metal cyanide anions present in the solution. Both Dowex 21K XLT and Amberjet 4600 had high exchange capacities and small functionalities which resulted in non-selective adsorption of all metal cyanide anions. This resulted in high loadings of iron, copper, nickel and zinc

on these two resins. Amberlite PWA-5 which had a lower exchange capacity and larger functionality, proved to have a higher affinity for the divalent metal cyanides in solution,  $Pt(CN)_4^{2-}$ ,  $Pd(CN)_4^{2-}$ ,  $Zn(CN)_4^{2-}$  and  $Ni(CN)_4^{2-}$  as opposed to the multivalent anions of  $Cu(CN)_4^{3-}$  and  $Fe(CN)_6^{4-}$ . The loading of the latter two metal cyanide anions could be reduced in continuous contact with fresh solution, which was caused by the divalent anions that displaced them on the resin. Minix had the lowest exchange capacity and largest functionality of all four resins, and was shown to have a high affinity for the monovalent aurocyanide anion,  $Au(CN)_2^-$ .

It was revealed in this study that pH and a temperature up to 60°C had no effect on the loading of platinum, palladium and gold. However, an improvement in the loading kinetics of platinum, palladium and gold was observed when the temperature of the solution was raised from 30°C to 60°C. An increase in the concentrations of zinc and nickel in solution decreased both the loading rate and loading of platinum, palladium and gold on the resins. From the investigation of the effect of platinum, palladium and gold concentrations, it can be concluded that an increase in the concentration of these metals significantly improved the loading and loading kinetics on the resins.

From the elution experiments it can be concluded that zinc cyanide and potassium thiocyanate can effectively elute platinum cyanide, palladium cyanide and aurocyanide from strong base anionic resins. Poor elution of platinum with the use of acidic thiourea was observed, and it was concluded that a kinetic effect on the reaction between  $Pt(CN)_4^{2-}$  and thiourea was caused by the acidic conditions of the eluting solution. Aurocyanide elution with the use of zinc cyanide and potassium thiocyanate also proceeded much more slowly than the elution of platinum cyanide and palladium cyanide.

Because of poor elution of platinum with the use of acidic thiourea, the eluant was eliminated from further investigation. It can be concluded that zinc cyanide and potassium thiocyanate proved to effectively elute all loaded metals cyanides from strong base anionic resins. However, due to rapid elution of base metal cyanides along with platinum cyanide and palladium cyanide, no split elution alternative was observed for both eluants, at the elution conditions investigated.

Overall the effective recovery of platinum, palladium and gold, from cyanide solutions containing low concentrations (< 1 ppm) of these metals is possible, with the use of strong base anionic resins. The selection of resins for this process is very important, because it was observed that different strong base resins showed different affinities for different metal cyanide anions in solution. The effective elution of all the metal cyanides from strong base anionic resins was possible with the use of zinc cyanide and potassium thiocyanate. Although acidic thiourea can effectively elute palladium and gold from the resins, poor elution of platinum was observed with the use of acidic thiourea. Thus this eluting

agent was eliminated from further investigation, because the aim of this project was to elute platinum, palladium and gold from the resins simultaneously, and not separately. However, acidic thiourea can prove to be valuable for a split elution between palladium and platinum because of the poor reaction kinetics associated with the reaction between  $Pt(CN)_4^{2-}$  and thiourea in acidic solutions.

## 8.2 Recommendations for Future Work

The use of ion exchange resins for the recovery of gold from cyanide solutions has been thoroughly studied for a few decades, and is well understood. The findings of this study have shown that effective recovery of platinum and palladium from cyanide solutions is also possible with the use of ion exchange resins. However, most of the work performed was done in batch mode, which is not sufficient for a scale-up and cost analysis.

To obtain this data, column loading experiments should be performed. The difficulty with this is the low concentration of platinum, palladium and gold in the solution. Low flow rates through the column are required to obtain the correct breakthrough of metals, however, when there is a low concentration of metals in solution, the experiment has to run for an extensive amount of time through a small amount of resin. However, column loading experiments can provide data on the actual loading that can be achieved on the resins, and should also indicate in what sequence the metals break through the column, which is a very important aspect for scale-up.

The loading of metals in continuous operation could not be determined, and thus for the elution experiments, the resins were loaded with pre-determined quantities of metals. The problem with this is that no relationship between loading and elution was established, but only the feasibility of the separate processes. Thus with column loading experiments, the relationship can be established, that could possibly lead to alternatives, such as acid washing, for the removal of base metals from the loaded resins prior to the elution of platinum, palladium and gold from the resins.

The work also showed that significant improvement in both the loading kinetics and loading of platinum, palladium and gold can be achieved with higher concentrations of these metals in the feed solution to the adsorption process. Thus methods to make the PLS more concentrated in platinum, palladium and gold prior to adsorption should be investigated, and can include alternatives such as a pre-concentration step, such as reverse osmosis, or a process such as the SART process that can reduce the base metal content in the PLS.

Finally a thorough cost-analysis should be performed on the process investigated, to compare it with other processes such as adsorption onto activated carbon and zinc

cementation.



# Bibliography

- Adams, M., G.J., M. and Hancock, R. (1987a). Models for the adsorption of aurocyanide onto activated carbon. Part II. Extraction of aurocyanide ion pairs by polymeric adsorbents. *Hydrometallurgy*, vol. 18, pp. 139 – 154.
- Adams, M., McDougall, G. and Hancock, R. (1987b). Models for the adsorption of aurocyanide onto activated carbon. Part III. Comparison between the extraction of aurocyanide by activated carbon, polymeric adsorbents and 1-phenol. *Hydrometallurgy*, vol. 19, pp. 95 – 115.
- Ageeva, I., Kolpakova, N., Kovyrkina, T., Potsyapun, N. and Buinovski, A. (2001). Mechanism and kinetics of the sorption of platinum, palladium and gold on activated carbon from uv-illuminated chloride solutions. *Analytical Chemistry*, vol. 56, no. 2, pp. 13 – 139.
- Allison, J. and Thompson, J. (1992 July). Process for the separation of precious group viii a metals from cyano complexes of such metals and other metals. Patent.
- Atwood, R. and Atwood, R. (1985). Design considerations for Merrill-Crowe plants. Tech. Rep. 58-385, Society of Mining Engineers of AIME.
- Aveston, J., Everest, D. and Wells, R. (1958). Adsorption of gold from cyanide solutions by anionic resins. *Chemical Society*, vol. 231.
- Barron, R. and Fritz, J. (1984). Effect of functional group structure on the selectivity of low capacity anion exchangers for monovalent anions. *Chromatography*, vol. 284, pp. 13 – 25.
- Barter, J., Lane, G., Mitchell, D., Kelson, R. and Dunne, R. and Trang, C. (2001). Cyanide management by SART. Technical Bulletin 2001 - 04, SGS Mineral Services.
- Bax, A. (2008 December). Recovery of platinum group metals. Patent.
- Chand, R., Watari, T., Inoue, K., Kawakita, H., Luitel, H., Parajuli, D., Torikai, T. and Yada, M. (2009). Selective adsorption of precious metals from chloride solutions using porous carbon prepared from barley straw and rice husk. *Minerals Engineering*, vol. 22, pp. 1277 – 1282.
- Chen, S., Xu, R., Huang, H., Yi, F., Zhou, X. and Zeng, H. (2007). Reduction-adsorption behaviour of platinum ions on activated carbon fibers. *Materials Science*, vol. 42, pp. 9572 – 9581.

- Christison, T. (2003). Direct determination of metal cyanides by ion chromatography with UV adsorbance detection. Application Update 147 LPN 1570 PDF 1/04, Dionex Corporation.
- Christopher, A., Stillian, J. and Jackson, P. (1997). Factors controlling ion-exchange selectivity in suppressed ion chromatography. *Chromatography A*, vol. 789, pp. 29 – 41.
- Clifford, D. and Weber, W. (1983). The determinants of divalent/monovalent selectivity in anion exchangers. *Reactive Polymers*, vol. 1, pp. 77 – 89.
- Conradie, P., Johns, M. and Fowles, R. (1995). Elution and electrowinning of gold from gold-selective strong-base resins. *Hydrometallurgy*, vol. 37, pp. 349 – 366.
- Cortina, J., Meinhardt, E., Roijals, O. and Marti, V. (1998). Modification and preparation of polymeric adsorbents for precious-metal extraction in hydrometallurgical processes. *Reactive and Functional Polymers*, vol. 36, pp. 149 – 165.
- Davis, W. (1880). Use of activated carbon for the precipitation of gold from solution and subsequent burning. Patent.
- Desmond, D., Atkinson, G., Kuczynski, R. and Walters, L. (1991). High-temperature cyanide leaching of platinum group metals from automobile catalysts - laboratory tests. Investigation 9384, U.S. Bureau of Mines.
- Dicinoski, G. (1994). *Syntheses of anion exchange resins selective for gold and silver cyanide complexes*. PhD, Central Queensland University, Department of Chemistry, Faculty of Applied Science.
- Eksteen, J., Mwase, J., Peterson, J., Bradshaw, S., Akdogan, G., Mpinga, N. and Snyders, N. (2012 June 18 - 20). A novel energy efficient process for the extraction of platinum group metals through a sequential stage high temperature heap leach process and subsequent recovery and elution using activated carbon. In: *Biohydrometallurgy '12*.
- Fleming, C. (1993). CIP and RIP: Where to next? In: Hiskey, J. and Warren, G. (eds.), *Hydrometallurgy Fundamentals, Technology and Innovation*.
- Fleming, C. (1998). The potential role of anion exchange resins in the gold industry. In: Mishra, B. (ed.), *Proceedings of EPD Congress*, pp. 95–117. Warrendale, PA: TMS.
- Fleming, C. and Cromberge, G. (1984a). The elution of aurocyanide from strong-and weak-base resins. *The South African Institute of Mining and Metallurgy*, vol. 84, no. 9, pp. 269–280.
- Fleming, C. and Cromberge, G. (1984b). The extraction of gold from cyanide solutions by strong-and weak-base anion exchange resins. *The South African Institute of Mining and Metallurgy*, vol. 84, no. 5, pp. 125 – 137.

- Fleming, C. and Cromberge, G. (1984c). Small-scale pilot-plant tests on the resin-in-pulp extraction of gold from cyanide media. *The South African Institute of Mining and Metallurgy*, vol. 84, no. 11, pp. 369 – 378.
- Gjerde, D. and Fritz, J. (1979). Effect of capacity on the behaviour of anion exchange resins. *Chromatography*, vol. 176, pp. 199 – 206.
- Green, B. (1988). Mechanism of loading of metal cyanides by weak-base resins. *Reactive Polymers*, vol. 8, pp. 221 – 234.
- Harris, W., Stahlbush, J., Pike, W. and Stevens, R. (1992). The extraction of gold from cyanide solutions using moderate base polyamine ion exchange resins. *Reactive Polymers*, vol. 17, pp. 21 – 27.
- Hiskey, J. (1983 October). Heap leaching practice at alligator ridge. In: *Current status of U.S. Gold and Silver Heap Leaching Operations, Heap and Dump Leaching practice*, pp. 1– 7. SME, Salt Lake City.
- Jermakowicz-Bartkowiak, D. and Kolarz, B. (2002). Gold sorption on weak base anion exchangers with aminoguanidyl groups. *European Polymer*, vol. 38, pp. 2239 – 2246.
- Jones, W., Klauber, C. and Linge, H. (1989). *Gold Forum on Technology and Practices - World Gold 89'*, chap. 32, pp. 278 – 281. ISBN 0-87335-085-5.
- Kargari, A., Kaghazchi, T., Sohradi, M. and Soleimani, M. (2004). Batch extraction of gold(III) ions from aqueous solutions using emulsion liquid membrane via facilitated carrier transport. *Membrane Science*, vol. 233, pp. 1 – 10.
- Kotze, M., Green, B., Mackenzie, J. and Virnig, M. (2005). Resin-in-pulp and resin-in-solution. *Developments in Mineral Processing*, vol. 15, pp. 603 – 635.
- Kuczynski, R., Atkinson, G. and Walters, L. (1992). High-temperature cyanide leaching of automobile catalysts in a process development unit. Investigation 9428, United States Bureau of Mines.
- Kwak, I., Bae, M., Won, S., Mao, J., Sneha, K., Park, J., Sathishkumar, M. and Yun, Y. (2010). Sequential process of sorption and incineration for recovery of gold from cyanide solutions: Comparison of ion exchange resin, activated carbon and biosorbent. *Chemical Engineering*, vol. 165, pp. 440 – 446.
- Lakshmanan, V. and Tackaberry, P. (1990 September). In: *Advances in Gold and Silver Processing*, chap. 25. Society for Mining, Metallurgy and Exploration.
- Lewis, G. and Bouwer, W. (2000). Resin-in-leach: An effective option for gold recovery from carbonaceous ores. In: *Randol International Gold and Silver Forum*, pp. 35 – 43. Randol International Ltd.

- Lukey, G., van Deventer, J. and Shallcross, D. (2000a). The effect of functional group structure on the elution of metal cyanide complexes from ion exchange resins. *Separation Science and Technology*, vol. 35, no. 15, pp. 2393 – 2413.
- Lukey, G., Van Deventer, J. and Shallcross, D. (2000b). Equilibrium model for the selective sorption of gold cyanide on different ion exchange functional groups. *Minerals Engineering*, vol. 13, no. 2, pp. 1243 – 1261.
- Marsden, J. and Fuerstenau, M. (1993). Comparison of Merrill-Crowe precipitation and carbon adsorption for precious metals recovery. In: *Proceedings of XVIII International Mineral Processing Congress*. Australian Institute of Mining and Metallurgy, Sydney, Australia.
- McDougall, G., Adams, M. and Hancock, R. (1987). Models for the adsorption of aurocyanide onto activated carbon. Part I: Solvent extraction of aurocyanide ion pairs by 1-pentanol. *Hydrometallurgy*, vol. 18, pp. 125–138.
- McDougall, G., Hancock, R., Nicol, M., Wellington, O. and Copperthwaite, R. (1980). The mechanism of the adsorption of gold on activated carbon. *South African Institute of Mining and Metallurgy*, vol. 80, pp. 344 – 356.
- McDougall, G.J. and Hancock, R. (1980). Activated carbons and gold - literature survey. *Minerals Science and Engineering*, vol. 12, pp. 85–99.
- McDougall, G.J. and Hancock, R. (1981). Gold complexes and activated carbon - a literature review. *Gold Bulletin*, vol. 14, pp. 138–153.
- Miller, J. (1984). Comparison of process alternatives for gold recovery from cyanide leach solutions. *SME/AIME*, pp. 93–107.
- Misak, N. (1993). Langmuir isotherm and its application in ion exchange reactions. *Reactive Polymers*, vol. 21, pp. 53 – 64.
- Moyer, B. and Singh, R. (2004). *Fundamentals and Applications of anion separations*. 1st edn. Kluwer Academic/ Plenum Publishers. ISBN 0-306-47911-7.
- Muhtadi, O. (1988). *Introduction to Evaluation, Design and Operation of Precious Metal Heap Leach Projects*, chap. 8, pp. 124 – 136. 1st edn. Society for Mining Metallurgy.
- Mwase, J., Peterson, J. and J.J., E. (2012). A conceptual flowsheet for heap leaching of platinum group metals (pgms) from a low-grade ore concentrate. *Hydrometallurgy*, vol. 111 -112, pp. 128 – 135.
- Nicol, M., Fleming, C. and Cromberge, G. (1984). The adsorption of gold cyanide onto activated carbon. I. The kinetics of adsorption from pulps. *South African Institute of Mining and Metallurgy*, vol. 84, no. 2, pp. 50 – 54.

- Niu, H. and Volesky, B. (1999). Characteristics of gold biosorption from cyanide solution. *Chemical Technology and Biotechnology*, vol. 74, pp. 778 – 784.
- Okeola, F. and Odeunmi, E. (2010). Comparison of Freundlich and Langmuir isotherms for adsorption of methylene blue by agrowaste derived activated carbon. *Advances in Environmental Biology*, vol. 4, no. 3, pp. 329 – 335.
- Oliveria, A., Leao, V. and da Silva, C. (2008). A proposed mechanism for nitrate and thiocyanate elution of strong-base ion exchange resins loaded with copper and gold cyanocomplexes. *Reactive and Functional Polymers*, vol. 68, pp. 141 – 152.
- O'Malley, G. (2002). *Recovery of gold from thiosulfate solutions and pulps with anion exchange resins*. PhD, Murdoch University, Perth, Australia.
- Petersen, F. and van Deventer, J. (1997). Competitive adsorption of gold cyanide and organic compounds onto porous adsorbents. *Separation Science and Technology*, vol. 32, no. 13, pp. 2087 – 2103.
- Riveros, P.A. (1993). Selectivity aspects of the extraction of gold from cyanide solutions with ion exchange resins. *Hydrometallurgy*, vol. 33, pp. 43 – 58.
- Roijals, O., Martf, V., Meinhardt, E., Cortina, J. and Aguilar, M. (1996). Characterization of spent automotive catalyst residues for precious metal recycling using hydrometallurgical technologies. *Chemical Industry and Environment*, vol. 2, pp. 419 – 428.
- Shams, K., Beiggy, M. and Shirazi, A. (2004). Platinum recovery from a spent industrial dehydrogenation catalyst using cyanide leaching followed by ion exchange. *Applied Catalysis A*, vol. 258, pp. 227 – 234.
- Sheintuch, M. (1981). A Freundlich-type multicomponent isotherm. *Colloid and Interface Science*, vol. 79, no. 1, pp. 136 – 142.
- Sibrell, P. and Atkinson, G. (1994). Cyanide leaching chemistry of platinum group metals. Presentation, Society for Mining, Metallurgy and Exploration.
- Sibrell, P. and Atkinson, G. (1995). Leaching of petroleum catalyst with cyanide for palladium recovery. Investigation 9535, U.S. Bureau of Mines.
- Staker, W. and Sandberg, R. (1997). Selective elution of mercury, silver and gold from strong base anion-exchange resins. Investigation 9093, United States, Bureau of Mines.
- Tetsuo, O. (1997). Nonaqueous anion exchange chromatography: Role of solvation in anion exchange resin. *Chromatography*, vol. 758, pp. 19 – 28.
- Van Deventer, J., Wyethe, J., Kotze, M. and Shannon, J. (1999 November). Comparison of resin-in-solution and carbon-in-solution for the recovery of gold from clarified solutions. In: *SAIMM Conference Metallurgy Africa*. South African Institute of Mining and Metallurgy.

- Van Vliet, B. (1991). The regeneration of activated carbon. *South African Institute of Mining and Metallurgy*, vol. 91, no. 5, pp. 159–167.
- Versiane, A. and Ciminelli, V. (2000). Application of ion exchange resins in gold hydrometallurgy. a tool for cyanide recycling. *Solvent Extraction and Ion Exchange*, vol. 18, no. 3, pp. 567 – 582.
- Woollacott, L., Stange, W. and King, R. (1990). Towards more effective simulation of CIP and CIL processes. 1. The modelling of adsorption and leaching. *South African Institute for Mining and Metallurgy*, vol. 90, no. 10, pp. 275 – 282.
- Zadra, J. (1950). Report of Investigations 4672, Bureau of Mines, Reno, Nevada.
- Zadra, J. (1952). Report of Investigations 4843, Bureau of Mines, Reno, Nevada.

# Appendices

# Appendix A

## Work Generated from this Thesis

### A.1 Conference Papers

Schoeman, E., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., The recovery of platinum, palladium and gold from a cyanide heap leach solution, with the use of ion exchange resins. Proceedings of The South African Institute of Mining and Metallurgy, Platinum 2012, Johannesburg, South Africa, September, 2012.

Schoeman, E., Bradshaw, S.M., Akdogan, G., Snyders, N., Eksteen, J.J., Extraction of platinum and palladium from a heap leach cyanide solution using strong base anion exchange resins. Accepted for the Proceedings of Minerals Engineering Conference, Precious Metals '12, Cape Town, South Africa, November, 2012.

Schoeman, E., Bradshaw, S.M., Akdogan, G., Snyders, N., Eksteen, J.J., Elution of platinum cyanide and palladium cyanide from strong base anion exchange resins. Accepted for the Proceedings of Minerals Engineering Conference, Precious Metals '12, Cape Town, South Africa, November, 2012.

### A.2 Submitted Journal Papers

Schoeman, E., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., Snyders, N., The extraction of platinum and palladium from a heap leach cyanide solution with the use of strong base anion exchange resins. Part I: Adsorption. Submitted to Hydrometallurgy, September, 2012.

Schoeman, E., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., Snyders, N., The extraction of platinum and palladium from a heap leach cyanide solution with the use of strong base anion exchange resins. Part II: Elution. Submitted to Hydrometallurgy, September, 2012.



## Appendix B

# Product Data Sheets for Selected Strong Base Anion Exchange Resins

Home : Products : Ion Exchange Resins : Strong Base Anion Exchange Resins : XZ 91419.00

### XZ 91419.00 Developmental Anion Resin

XZ 91419.00 is a developmental strong base anion exchange resin for gold recovery in mining applications (manufactured under license from MINTEK).

Type	Matrix	Functional Group
t-Butylamine	Styrene-DVB, Gel	Quaternary Amine

Guaranteed Sales Specification	Units	
Total Exchange Capacity, min.	eq/L	0.23 - 0.33
Dry Weight Capacity	meq/g	0.8 - 1.2
Water Retention Capacity	%	45 - 55
Particle Size Distribution		
Range	µm	760 - 1200
> 1190 µm, max.	%	2
< 768 µm, max.	%	5

Typical Physical and Chemical Properties	Units	
Not to be construed as Sales Specifications		
Particle Density	g/mL	1.08
Shipping Weight**	g/L	670
	lbs/ft <sup>3</sup>	42

Figure B.1: Data sheet for Minix

**ROHM|HAAS** | Drinking Water

## PRODUCT DATA SHEET

**AMBERLITE™ PWA5 Resin****Drinking Water Grade****Nitrate Selective**

AMBERLITE PWA5 resin is a strongly basic anion exchange resin, developed for selective nitrate removal from drinking waters. AMBERLITE PWA5 resin removes nitrate preferentially to sulfate, and therefore can yield operating capacity higher than conventional resins.

These characteristics make AMBERLITE PWA5 resin the perfect choice for a simple, regenerable nitrate removal process for municipal water treatment.

AMBERLITE PWA5 resin is compatible with the Advanced Amberpack™ Municipal system.

**PROPERTIES**

Matrix	Cross linked copolymer	
Physical form	Cream beads	
Total exchange capacity	≥ 1.0 eq/L	
Moisture holding capacity	52 – 58%	
Shipping weight	690 kg/m <sup>3</sup>	(43 lb/ft <sup>3</sup> )
Particle size		
Screen grading	0.3 – 1.2 mm	(16 – 50 mesh US Std Screens)
Fines content	<0.300 mm: 0.3% max	

**SUGGESTED OPERATING CONDITIONS**

Please contact your Rohm and Haas representative for system design and application testing details.

Maximum operating temperature	75 °C	(170 °F)
Minimum bed depth	610 mm	(24 inches)
Typical service flow rate	5 – 40 BV/h*	(0.6 – 5 gpm/ft <sup>2</sup> )
<b>Regenerant (100% basis)</b>	<b>NaCl</b>	
Concentration	6 – 12%	
Minimum level	80 g/L	(5 lbs/ft <sup>3</sup> )
Minimum contact time	20 minutes	

\* 1 BV (Bed Volume) = 1 m<sup>3</sup> solution per m<sup>3</sup> resin

**COMMISSIONING AND LIMITS OF USE**

AMBERLITE PWA5 resin is suitable for use in potable water applications after performing a full regeneration cycle at a dosage of 120 g of NaCl per liter of resin followed by an adequate rinse to remove excess of brine.

The operating capacity of AMBERLITE PWA5 resin depends on the operating conditions and the feed water conditions.

**REGULATORY**

AMBERLITE PWA5 resin is certified to ANSI/NSF Standard 61 for drinking water components. AMBERLITE PWA5 resin is approved for use in public water supplies in the UK. Please contact your Rohm and Haas representative for additional certification information.

**Figure B.2:** Data sheet for Amberlite PWA-5

## AMBERJET™ 4600 Cl

### Industrial Grade Strong Base Anion Exchanger

AMBERJET 4600 Cl resin is a uniform particle size, high quality, strong base type 2 anion exchanger designed for use in all general demineralisation systems. The uniformity and mean particle size of AMBERJET 4600 Cl resin have been optimised for

use in industrial equipment including co-flow, reverse flow regenerated units and packed bed systems. It can be directly substituted for conventional gel anion exchange resin in new equipment and in rebeds of existing demineralisers.

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#### PROPERTIES

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Physical form _____	Yellow translucent spherical beads
Matrix _____	Styrene divinylbenzene copolymer
Functional group _____	Dimethyl ethanol ammonium
Ionic form as shipped _____	Cl <sup>-</sup>
Total exchange capacity <sup>(1)</sup> _____	≥ 1.25 eq/L (Cl <sup>-</sup> form)
Moisture holding capacity <sup>(1)</sup> _____	45 to 51 % (Cl <sup>-</sup> form)
Specific gravity _____	1.085 to 1.115 (Cl <sup>-</sup> form)
Shipping weight _____	680 g/L
Particle size	
Uniformity coefficient <sup>(1)</sup> _____	≤ 1.25
Harmonic mean size _____	0.60 to 0.80 mm
< 0.425 mm <sup>(1)</sup> _____	0.5 % max
Maximum reversible swelling _____	Cl <sup>-</sup> → OH <sup>-</sup> : 20 %

<sup>(1)</sup> Contractual value

Test methods available upon request

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#### SUGGESTED OPERATING CONDITIONS

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Maximum operating temperature _____	35 °C
Minimum bed depth _____	800 mm
Service flow rate _____	5 to 50 BV*/h
Maximum service velocity _____	60 m/h
Regeneration	
Regenerant _____	NaOH
Level _____	30 to 100 g/L
Concentration _____	2 to 5 %
Minimum contact time _____	20 minutes
Slow rinse _____	2 BV at regeneration flow rate
Fast rinse _____	3 to 6 BV at service flow rate

\* 1 BV (Bed Volume) = 1 m<sup>3</sup> solution per m<sup>3</sup> resin

Figure B.3: Data sheet for Amberjet 4600

**DOWEX 21K XLT**

A Uniform Particle Size, High Capacity, Strong Base Anion Exchange Resin for Mineral Processing Applications

Product	Type	Matrix	Functional group
DOWEX® 21K XLT	Type I strong base anion	Styrene-DVB, gel	Quaternary amine

**Guaranteed Sales Specifications**

Total exchange capacity, min.	eq/L	1.4
Water content	%	50 - 60
<b>Bead size distribution</b>		
Volume median diameter	µm	525 - 625
Uniformity coefficient, max.	%	1.1

**Typical Physical and Chemical Properties**

Ionic form as delivered		Cl <sup>-</sup>
Total swelling (Cl <sup>-</sup> ⇒ OH <sup>-</sup> ), approx.	%	18 - 20
Whole uncracked beads, min.	%	90
Particle density, approx.	g/mL	1.08
Shipping weight, approx.	g/L lbs/ft <sup>3</sup>	670 42

**Recommended Operating Conditions**

- Maximum operating temperature:  
OH<sup>-</sup> form 60°C (140°F)  
Cl<sup>-</sup> form 100°C (212°F)
- pH range 0 - 14
- Bed depth, min. 800 mm (2.6 ft)
- Flow rates:  
Service/fast rinse 5 - 60 m/h (2 - 24 gpm/ft<sup>2</sup>)  
Backwash See figure 1  
Co-current regeneration/displacement rinse 1 - 10 m/h (0.4 - 4 gpm/ft<sup>2</sup>)  
Counter-current regeneration/displacement rinse 5 - 20 m/h (2 - 8 gpm/ft<sup>2</sup>)
- Total rinse requirement 3 - 6 Bed volumes
- Regenerant:  
Type NaCl/Carbonate  
Temperature Ambient or up to 50°C (122°F) for silica removal
- Organic loading, max. 3g KMnO<sub>4</sub>/L resin

Figure B.4: Data sheet for Dowex 21K XLT