

**Western Australian School of Mines
Department of Mining Engineering and Metallurgical Engineering**

Extraction of PGMs from Low-grade Oxide Mineral Deposits

Cleophace Ngoie Mpinga

**This thesis is presented for the Degree of
Doctor of Philosophy
of
Curtin University**

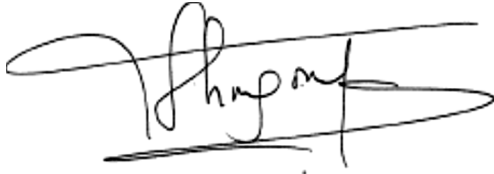
July 2018

DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Date: Saturday 07 July 2018

A handwritten signature in black ink, appearing to read 'Cleophas Ngou Mpinga', written in a cursive style with a large initial 'C' and a long horizontal stroke extending to the right.

Cleophas Ngou Mpinga.

ABSTRACT

The fast depletion of sulfide PGM-bearing minerals and the deteriorating socio-political environments in most primary PGM producing countries have triggered interest in exploring the recovery of these metals from high-chromium PGM-bearing oxidized ores — sometimes containing relatively high marketable PGM values — which have proven to be more difficult to process by conventional metallurgical practice which involves grinding, milling, froth flotation into a sulfide concentrate, smelting and matte production and chemical refining.

In general, the processing of high-chromium oxidized ores by conventional flotation techniques typically results in very poor concentrate grade and PGM recoveries. Previous attempts have proved uneconomic due to low recoveries ($\ll 50\%$) achieved by conventional metallurgical methods. Hence if an oxide ore cannot be preconcentrated, the treatment method will have to accommodate large volumes of relatively low-grade material containing PGMs in a wide variety of mineral forms that cause hydrometallurgical processes to be inappropriate. At present, oxide ores are either left *in-situ*, stockpiled or discarded as waste.

There has been some considerable research aimed at improving flotation recoveries of oxidized PGM ores by employing techniques such as 1) controlled potential sulfidization prior to flotation, 2) acid pretreatment of ores before flotation and 3) the use of various flotation reagent schemes. Besides these techniques, direct leaching approaches have also been tested, where sperrylite has been found to be the main residual platinum bearing mineral remaining undissolved.

The point of departure of this research project is a prior patented process, called the “Panton process” that was developed for the high-chromite oxidized Panton sill deposit as the two-staged mill-float-mill-float circuit (MF2) was developed for the South African chromite-rich unoxidized deposits. The deficiencies of the Panton process is discussed leading up to the development of a novel process chemistry (non-smelting) and flowsheet that should be applicable to a broad range of PGM-bearing oxide ores.

This research was executed by publishing four peer-reviewed journal articles. It explored extraction routes to recover metal values from PGM-bearing chromite ores containing mostly oxide minerals, platinum as sperrylite and palladium as

antimonide. Process conditions included ambient pressure and air as atmosphere, without need to add further oxidizing agents. A hybrid pyro-hydrometallurgical process has been developed and evaluated.

Solution streams are typically recycled and reagents are regenerated. This provides definite advantages in terms of reduced plant effluents, reduced operating costs and improved plant water balance. With the development of such flowsheet herein by The Western Australian School of Mines, substantial PGM recoveries from oxide and mixed oxide/sulfide ores are now possible, in other words the technique is not limited to just Panton Sill deposit ore. The technique is expected to be a direct treatment route from flotation concentrate or ore to PGM refinery feed.

ACKNOWLEDGEMENTS

First and foremost, Praises to my Heavenly Father and to my Lord and Saviour Jesus Christ. The Cornerstone of any Major construction and Source of all grace, for giving me the health, strength and ability to write this thesis. This is the fulfilment of Your Prophecies. You are the Greatest Engineer of all. Everything I have is a blessing from You Lord. Without You my life is meaningless.

Special thanks to my supervisors Prof. Jacques Eksteen, Prof. Chris Aldrich and Dr. Laurence Dyer for your guidance, patience and untiring efforts during the last four years. Your advices and supports were instrumental in the successful completion of this project. It has been a great privilege to spend all these years at WASM/Bentley campus, all its members and memories always remain in my mind.

This research project was initiated and sponsored by Panoramic Resources Ltd. and the Minerals Research Institute of Western Australia (MRIWA Grant M458). Their financial support is kindly acknowledged with appreciation. I'm also grateful for the financial support provided by the Curtin International Postgraduate Research Scholarships (CIPRS) at Curtin University in Perth, Western Australia.

LIST OF PUBLICATIONS INCLUDED AS PART OF THE THESIS

The PhD student conducted all the tests and wrote the manuscripts. The following peer-reviewed journal publications related to the work are modest contribution by the candidate to scientific knowledge and development during his doctoral candidacy between June 2014 and June 2018.

- I. **Mpinga, C.N.**, Eksteen, J.J., Aldrich, C., Dyer, L., 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review. *Minerals Engineering* 78, 93-113.
- II. **Mpinga, C.N.**, Eksteen, J.J., Aldrich, C., Dyer, L., 2017. Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore. *Minerals Engineering* 110, 153-165.
- III. **Mpinga, C.N.**, Eksteen, J.J., Aldrich, C., Dyer, L., 2018a. Atmospheric leach process of high-chromitite PGM-bearing oxidized mineralized ore through a single-stage and two-stage techniques. *Minerals Engineering* 125, 165-175.
- IV. **Mpinga, C.N.**, Eksteen, J.J., Aldrich, C., Dyer, L., 2018b. A conceptual hybrid process flowsheet for platinum group metals (PGMs) recovery from a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization through a single-stage leach and adsorption onto ion exchange resin. *Hydrometallurgy* 178, 88-96.

"I warrant that I have obtained, where necessary, permission from the copyright owners to use any third-party copyright material reproduced in the thesis (e.g. questionnaires, artwork, unpublished letters), or to use any of my own published work (e.g. journal articles) in which the copyright is held by another party (e.g. publisher, co-author)."

STATEMENT OF CONTRIBUTION OF OTHERS

The PhD candidate conceived, designed, performed the experiments, analysed and interpreted the experimental data and wrote all four peer-reviewed journal papers forming body of this thesis by publication. The author of this dissertation is the first author in all listed publications. Prof. Jacques Eksteen, Prof. Chris Aldrich and Dr. Laurence Dyer were responsible for editing and revising the manuscripts. Signed detailed statement is provided as appendix (A) at the back of this volume.

**LIST OF ADDITIONAL PUBLICATIONS BY THE CANDIDATE RELEVANT
TO THE THESIS BUT NOT FORMING PART OF IT**

- I. **Mpinga, C.N.**, 2012. The extraction of precious metals from an alkaline cyanided medium by granular activated carbon. MSc Thesis, University of Stellenbosch, Faculty of Engineering, South Africa.
- II. **Mpinga, C.N.**, Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2014. The extraction of Pt, Pd and Au from an alkaline cyanide simulated heap leachate by granular activated carbon. *Minerals Engineering* 55, 11-17.
- III. **Mpinga, C.N.**, Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2014. Evaluation of the Merrill-Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solutions. *Hydrometallurgy* 142, 36-46.
- IV. Snyders, C.A., **Mpinga, C.N.**, Bradshaw, S.M., Akdogan, G., Eksteen, J.J., 2012. The adsorption and elution of platinum group metals (Pt, Pd, and Au) from cyanide leach solutions using activated. *The Southern African Institute of Mining and Metallurgy Platinum* 2012.
- V. Eksteen, J.J., Mwase, J.M., Petersen, J., Bradshaw, S.M., Akdogan, G., **Mpinga, C.N.**, Snyders, C.A., 2012. A novel energy efficient process for the extraction of platinum group metals through a sequential stage high temperature heap bioleach and subsequent high temperature cyanide heap leach utilising solar heat. *Biohydrometallurgy*, 2012.
- VI. Snyders, C.A., **Mpinga, C.N.**, Bradshaw, S.M., Akdogan, G., Eksteen, J.J., 2013. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions. *The Journal of the Southern African Institute of Mining and Metallurgy* 113, 381-388.
- VII. Snyders, C., Bradshaw, S., Akdogan, G., **Mpinga, C.N.**, Wyk, A., Eksteen, J., 2014. Recovery of Pt, Pd and Au from a cyanide solution through a carbon adsorption and elution process. In *IMPC 2014-27th International Mineral Processing Congress*. Gecamin.

- VIII.** Eksteen, J.J., Mwase, J.M., Petersen, J., Bradshaw, S.M., Akdogan, G., **Mpinga, C.N.**, Snyders, C.A., 2014. A novel, energy efficient, two stage heap leach process for the extraction and recovery of PGMs. Proceedings of the XXVII International Mineral Processing Congress. 19-24 October 2014, Santiago, Chile. pp. 20-24.

DEDICATION

This work is dedicated to my beautiful wife Francine Kabanga Mushiya and our four dearly beloved children: Celine Kabola Mpinga, Herman Mpoyi Mpinga, Adonay Kabedi Mpinga and Benita Ciani Mpinga for their understanding, patience, spiritual and moral support during the course of this doctoral journey. I appreciate it more than you know.

Work hard and become a leader; be lazy and become a slave (Proverbs 12:24).

God bless you.

TABLE OF CONTENTS

DECLARATION	I
ABSTRACT	II
ACKNOWLEDGEMENTS	IV
LIST OF PUBLICATIONS INCLUDED AS PART OF THE THESIS	V
STATEMENT OF CONTRIBUTION OF OTHERS	VI
LIST OF ADDITIONAL PUBLICATIONS BY THE CANDIDATE RELEVANT TO .	VII
DEDICATION	IX
TABLE OF CONTENTS	X
CHAPTER I : GENERAL INTRODUCTION AND OVERVIEW	1
I.1 . BACKGROUND — EXPLANATORY OVERVIEW.....	3
I.2 . OBJECTIVES OF THE STUDY.....	5
I.3 . RESEARCH QUESTIONS	5
I.4 . SIGNIFICANCE OF THE STUDY	6
I.5 . DELINEATION OF THE STUDY	6
I.6 . THESIS ORGANIZATION.....	7
I.7 . OVERALL CONCLUSIONS	10
I.8 . RECOMMENDATIONS AND FUTURE RESEARCH OPPORTUNITIES.....	11
I.9 . REFERENCES	12
CHAPTER II : LITERATURE REVIEW	15
CHAPTER III : SULFURIC ACID BAKE PROCESS AT 550°C	38
CHAPTER IV : SULFURIC ACID AND MOLTEN SALTS CHLORINATION	53
CHAPTER V : PRACTICAL APPROACH TO PGMS RECOVERY FROM	66
APPENDICES	77
APPENDIX A: SIGNED STATEMENT OF CONTRIBUTION OF CO-AUTHORS. ..	78
APPENDIX B: AT FIRST HAND EQUIPMENT USED IN THIS THESIS.	80
B1. EQUIPMENT USED AT ROASTING STAGE	81
B2. EQUIPMENT USED AT LEACHING STAGE	82
B3. EQUIPMENT USED AT ADSORPTION AND ELUTION STAGES	83
APPENDIX C: CERTIFICATE OF ORIGIN AND ANALYSIS — SAFETY DATA SHEET OF WEAK-BASE ANION EXCHANGE RESIN DEAE CELLULOSE	84
APPENDIX D: SUPPORTING CALCULATIONS DERIVED FROM SYNTHETIC STOCK SOLUTIONS PREPARATION	93
APPENDIX E: TABULATION OF EXPERIMENTAL DATA.	97
BIBLIOGRAPHY	123

CHAPTER I : GENERAL INTRODUCTION AND OVERVIEW

SUMMARY

This Chapter provides a summary, an introduction to the research work presented in the thesis. It describes the research background and explains the motivation for pursuing the work. Research objectives and interconnections between Chapters are presented. The Chapter also summarizes major findings of the entire research study, which are of both scientific and practical interest. Recommendations for future research opportunities are also listed.

I.1. BACKGROUND — EXPLANATORY OVERVIEW

Mpinga et al. (2018b) stated that the availability of oxidized platinum group metal (PGM) ore deposits, at or near the earth's surface, present lucrative prospects for future PGM production owing to the large resource estimates, the relatively high PGM grades and they can be mined through relatively lower-cost open-pit mining processes. However, these oxidized PGM ores are currently not mined or treated due to insufficient recoveries using established metallurgical techniques (Kraemer et al., 2015; Becker et al., 2014; Bulatovic, 2003). The complex mineralogy and polymodal distribution of PGM in the oxidized ores pose a number of challenges to the metallurgist from a mineral liberation and extraction perspective (Kraemer et al., 2017).

In general, the processing of high-chromium oxidized ores by conventional flotation techniques typically results in very poor concentrate grade and PGM recoveries (Mpinga et al., 2018b; Becker et al., 2014; Lewins and Greenaway, 2004; Bulatovic, 2003). Previous attempts to extract PGMs from such ore type have proved uneconomic due to low recoveries ($\ll 50\%$) achieved by conventional metallurgical methods (Oberthür et al., 2013). Hence if an oxide ore cannot be preconcentrated, the method of treatment will have to accommodate large volumes of relatively low-grade material containing PGMs in a wide variety of mineral forms (Evans, 2002) that cause hydrometallurgical processes to be inappropriate. At present, oxide ores are either left *in-situ*, stockpiled or discarded as waste (Oberthür et al., 2013).

It is evident from previously reported literature that there has been some considerable research aimed at improving flotation recoveries of oxidized PGM ores by employing techniques such as 1) controlled potential sulfidization prior to flotation (Kalichini et al., 2017; Becker et al., 2014; Lee et al., 2009; Newell et al., 2006), 2) acid pretreatment of ores before flotation (Luszczkiewicz and Chmielewski, 2008) and 3) the use of various flotation reagent schemes (Becker et al., 2014; Lee et al., 2009; Bulatovic, 2003; Lee et al., 1998; Assis et al., 1996). Besides these techniques, direct leaching approaches have also been tested, where sperrylite has been found to be the main residual platinum bearing mineral remaining undissolved (Mpinga et al., 2017; Shaik and Petersen, 2017; Sefako et al., 2017; Mwase and Petersen, 2017; Mwase et al., 2014, 2012a, 2012b; Kraemer et al., 2015).

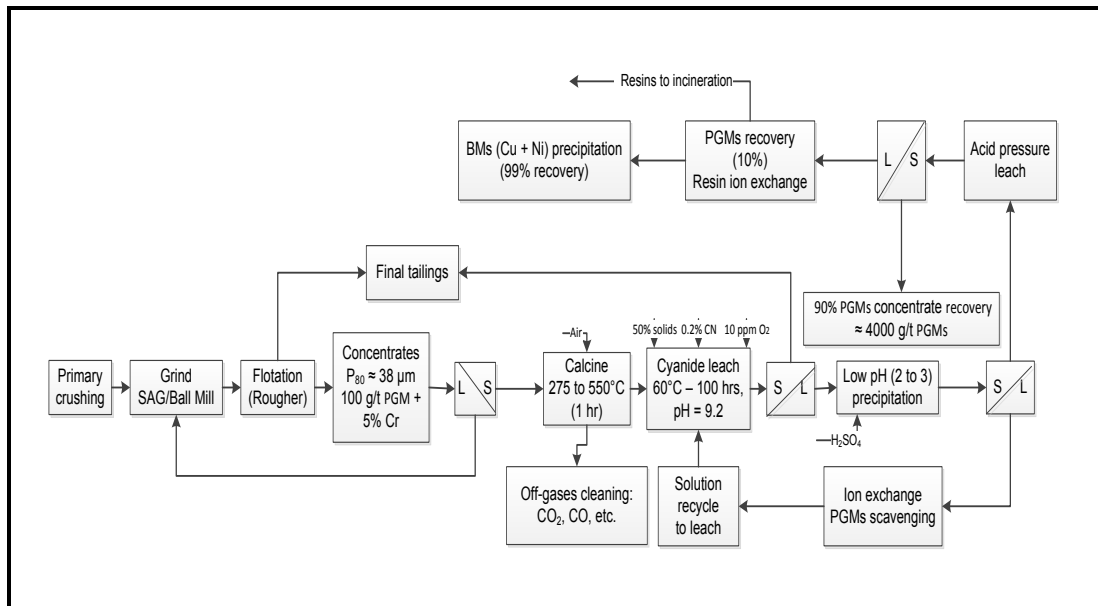


Figure I-1: Panton process conceptual flow schematic (Lewins and Greenaway, 2004)

Platinum Australia Limited (PLA) in conjunction with Lonmin Plc. have developed a process that used roasting and hydrometallurgical techniques to extract metal values from PGM-bearing chromite ores in oxidized mineralization (Bax et al., 2009). For the purposes of further reference, this process will be referred to as the “Panton process” (Figure I-1) which has been described at high level by Lewins and Greenaway (2004). The process proposes a complex recovery route using a combination of Calcination Cyanidation — Low pH precipitation and Acid pressure oxidative leach (Mpinga et al., 2017).

According to Mpinga et al. (2017), the overall process suffers from several shortcomings such as, long leaching time i.e. slow leaching rate, unexplained precipitation and redissolution steps, high reagent consumption due to reacting base metal sulfides, loss of platinum to tailings (platinum content mineralized as sperrylite), unacceptable level of safety risks of HCN gas release due to cross contamination as well as the suggestion of a pressure leach of its own created precipitate (sludge) and an inherently complex flowsheet, which provided a reasonable and useful starting point for the current research project. Hence alternative hydrometallurgical or hybrid pyro-hydrometallurgical routes using noncyanide lixiviants such as thiocyanate and chlorides were envisaged.

I.2. OBJECTIVES OF THE STUDY

From the literature review, it was apparent that much research has been and is still being devoted to the performance of gold acid leaching by SCN^- solutions (which served as a reference) and how to improve such performance (Li et al., 2012a, 2012b; Wan and LeVier, 2011; Kuzugüdenli and Kantar, 1999). To the best of our knowledge, there was no reliable data available in open literature on platinum group metals (PGMs) leaching behaviour using such solutions.

Based on the ability of platinum group metals to form stable thiocyanato-complexes in acidic solutions, a single or a two-stage leach process to extract base and precious metals — at atmospheric pressure — from the complex, chromite-rich Cu-Ni-PGM oxidized ore from Panton Sill deposit was suggested. This constituted the prime objective, with open minds to select new paths in the research field, in case such technique fails to provide satisfactory recoveries. Halide based processes can therefore also be considered, should processes be found that are sufficiently selective and excludes the use of gaseous halides.

As sperrylite is a dominant platinum-bearing mineral found in many of the world's largest PGM deposits, more emphasis was placed on it, owing to its reputation of being more refractory towards oxidation/dissolution in comparison with other precious metals. Furthermore if the solubilization of PGMs proved effective, and as an added bonus for this thesis, the second objective was to find a successful process which enables their recoveries from the leachates.

I.3. RESEARCH QUESTIONS

The objectives of the current study were encompassed in the following research questions — some of which were generic, and some project specific — that needed to be addressed.

1. Which aspects should be considered for a successful and efficient leaching of PtAs_2 , especially when it is contained in oxidized mineralization?
2. Are the PtAs_2 temperature-driven structural changes occurring through roast at 550°C or higher playing an important role in its solubilization in sulfuric thiocyanate solutions?
3. Is HCl feasible for dissolving and stabilizing PGM containing materials?
4. Can the *in-situ* generation method of Cl_2 provide enough ingredients for PtAs_2/Pt dissolution?

5. Is it possible to design a recovery process that selectively retains trace quantities of precious metals, while leaving the large excess of base metals and other contaminating metals ions in the effluent, so as to avoid the use of an excessively large amount of adsorbent(s)?
6. What will be the loading capacity(ies) of such adsorbent(s) toward PGMs?
7. What will a conceptual flowsheet look like that would utilise the outcomes from this research?

I.4. SIGNIFICANCE OF THE STUDY

This investigation would be a breakthrough in processing stranded deposits or difficult-to-treat refractory PGM-bearing materials in oxidized mineralization (Kraemer et al., 2017, 2015; Oberthür et al., 2013; Evans, 2002). In addition, low-grade mineralized wastes — often below the cut-off grade for conventional process that could not generate a positive operating profit — can also be processed. Finally according to Green et al. (2004), an extra 2 to 3% of PGMs might be recovered if 10% of chromite (from unoxidized ores) was allowed into the concentrate used in the traditional matte–smelting–refining technique.

Furthermore, this work constitutes a valuable contribution to the understanding of factors that need to be considered during any leaching investigation of refractory platinum group minerals in complex mineralogical systems. The research project will provide researchers with experimental values, which will be useful for pilot scale testing, as well as contribute to the academic discourse and debate within this discipline.

Also, it was foreseen that the use of low-temperature leaching at atmospheric conditions, would result in substantially lower capital and operating costs, than other technologies such as the traditional matte–smelting–refining technique, the conventional HCl/Cl₂ chlorination treatment system or any other two-stage leach process. In other words, the potential technology from this investigation is expected to be a direct treatment route from flotation concentrate or, in some cases, even the ore itself to PGM refinery feed.

I.5. DELINEATION OF THE STUDY

The research was limited to the processing of the refractory run-of-mine PGM-bearing ore in oxidized mineralization from Pantón Sill deposit. Findings from this processing might be successfully applied to concentrates and other less refractory

materials. Ideally the potential process should be applied on low-grade rougher concentrate at high flotation mass pull e.g. 10% as compared to the usual 2% (Mwase et al., 2014). Note that effluents from the expected process and its materials of construction are two factors significant enough to render the process flowsheet infeasible. However, these will not be dealt with as they are beyond the intended scope of this thesis.

I.6. THESIS ORGANIZATION

This thesis is written in article format with references listed according to the specific referencing style of the publishing journal. The dissertation is in full compliance with Curtin University copyright policies and specific guidelines for thesis by publication. The materials and methods for each part of the study are explained in the relevant Chapters. The thesis main body is subdivided into five interconnected Chapters and five appendices. It has the following sequential and outlining development layout:

➤ CHAPTER I: GENERAL INTRODUCTION AND OVERVIEW

This Chapter serves as an overall introduction. It presents the summary of problems arising from the previous work, the overall objectives for this study and also delineates the research that was done. Chapter I pinpoints the gaps in the scientific knowledge and hypotheses for future research.

➤ CHAPTER II: LITERATURE REVIEW

Chapter II (published paper I: Mpinga et al., 2015) is essentially a comprehensive review of some of the most recent literature on the predominantly hydrometallurgical approaches to PGM extraction. A number of metallurgical processes that generate either a PGM-rich leachate or a residue containing metal values, and the various methods in use for their recoveries from pregnant-rich solutions were reviewed. Sixteen process flowsheet variants combining conventional and proprietary unit process technologies were provided. Their process chemistries and key technical operating parameters were compared. Where appropriate, the key thermodynamic and kinetic factors were given and compared (Mpinga et al., 2015).

➤ CHAPTER III: SULFURIC ACID BAKE PROCESS AT 550°C

The roasting stage in the "Panton process" flowsheet (Figure I-1) was localized as a strategic entry point for inducing transformations to the sperrylite refractory structure. This Chapter (published paper II: Mpinga et al., 2017) determines whether the introduction of a sulfation roast pretreatment step (instead of conventional

oxidation roasting) to break down the crystal lattices, thereby rendering copper and nickel containing phases amenable to water leaching, would result in their recoveries and simultaneously concentrating platinum metals in a solid residue. Chapter III presents findings of preliminary sulfation bake tests, outlining the effect of roasting temperature on PtAs₂ oxidation behaviour.

However, the mineralogical characterization unfortunately still identified the presence of sperrylite in the water leach residues following the roast at 550°C, which is the highest temperature in the “Panton process” mentioned by Lewins and Greenaway (2004). Whereas, any pretreatment option should include a feasible strategy to further extract PGMs, the roasting process requires high temperatures to break down or decompose the crystal lattices to fully expose them to an appropriate leaching reagent. This observation paved the way for the next Chapter i.e. published paper III: Mpinga et al., 2018a.

➤ **CHAPTER IV: SULFURIC ACID AND MOLTEN SALTS CHLORINATION BAKE PROCESSES AT 650°C**

1. Sulfuric acid bake

A higher roast temperature of 650°C was investigated in this Chapter to ensure sperrylite would decompose. This was based on the assumption that increasing the roast temperature above the As-Pt eutectic of 597°C (Okamoto, 1990), would enable the arsenic to be released. Its concentration in the calcined ore was reduced from 185 to less than 0.5 g/t. Mineralogical examination confirmed sperrylite had decomposed.

Base metals beneficiation by sulfation roast was in principle straightforward (Mpinga et al., 2018a, 2017). The results showed that the extent and rate of Cu extraction were higher than Ni reaching 85% within 30 minutes. The use of acidified water facilitated almost complete Cu extraction. Nickel dissolution, on the other hand, reached 92.1% after 24 hours. However, the difficulty lied in further processing of sulfuric acid first campaign leach residue for PGMs dissolution. The primary leach residue was leached in sulfuric acid with thiocyanate at 50 and 85°C in the presence and absence of iodide as a catalyst. Pt in all cases failed to leach (< 0.2%) and less than 40% of the Pd was extracted.

No matter the temperature, the extraction of palladium quickly plateaued after 4 hours and lower extraction was observed in the presence of iodide. This poor

performance was attributed to additional iron dissolution in the second leach (~45%) which is likely to have precipitated as a jarosite (iron hydroxide) (Broadhurst and Du Perez, 1993) and would possibly passivate the surface. According to Dutrizac (1983), jarosite-type compounds have the ability to precipitate iron from acidic leach solutions.

The actual reason for the mixed ligand system performing poorly is unclear and requires further investigation. Therefore the $\text{H}_2\text{SO}_4\text{-SCN(I)}$ leach approach was found not fit-for-purpose. As elaborated in Chapter V (published paper IV: Mpinga et al., 2018b), thiocyanate usage should be restricted to PGM adsorption processes rather than ore leaching.

2. Molten salts chlorination bake

To our best knowledge, chlorine gas is required to improve the extraction in a two-stage leach process (Liddell and Adams, 2012; Tatarnikov et al., 2004). PGM-bearing concentrates are leached under aggressive conditions in a HCl/Cl_2 medium (Sole et al., 2005). The HCl/Cl_2 leach approach is not suitable for low-grade ores or concentrates, but rather highly concentrated PGM feedstocks as found in PGM refineries. Although the direct use of chlorine gas was not considered in this work, similar aggressive leach conditions could be indirectly created through the pyrohydrolysis of some low-cost and readily available chlorinating salts.

Hence instead of sulfation bake, a molten salts chlorination bake process performed at 650°C , which lies just below the temperatures at which copper and nickel ferrites form (670 and 764°C , respectively) and just above the temperatures (500 to 600°C) at which PtAs_2 starts to decompose (Muir and Ariti, 1991; Okamoto, 1990) would be appropriate to volatilize and remove arsenic in the off-gas stream or as a calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$ compound. This Chapter (published paper III: Mpinga et al., 2018a) presents and discusses the outcomes gained from both baking studies. It also provides the recovery mechanism of platinum from PtAs_2 .

➤ CHAPTER V: PRACTICAL APPROACH TO PGMs RECOVERY FROM ORES IN OXIDIZED MINERALIZATION AND SUBSEQUENT LEACHATES

Although PGMs solubilization was an important measure of the overall processing method success, the degree to which these are recovered from pregnant solutions is equally important. This recovery attempt has led to additional broadening of the

investigation scope, but still maintaining consistency with the main proposals of the study.

This Chapter (published paper IV: Mpinga et al., 2018b) examined under laboratory batch-scale conditions, the technical feasibility of using commercially available anion exchanger diethylaminoethyl cellulose (DEAE) for the separation and preconcentration of Pt(IV) and Pd(II) from very large volumes of base metal and other common accompanying ions.

Effects of various variables — such as equilibration time, thiocyanate and tin chloride concentrations — that might influence the adsorption process performance were studied. The uptake of Pt(IV) and Pd(II) onto the resin was successfully accomplished with recovery rates averaging 100% within the first 15 minutes. The addition of SCN^- to the iron chloride containing leachate (ligand exchange reaction) served as a preconcentration step for trace PGM components prior to their recovery.

The results indicated a very rapid increase in platinum extraction from 67.05% at zero SCN(I) concentration to a maximum of 100% at 0.58 M SCN(I) , with which 99.95% of the palladium was extracted. Irrespective of leach liquor Sn(II) content, tests with virgin and presoaked resins gave 100% adsorption of both Pt(IV) and Pd(II) in presence of SCN(I) .

Thiourea proved to be better stripping reagent for bulk elution of combined Pd(II) and Pt(IV). Thereby, a conceptual flowsheet was disclosed for hydrometallurgical pilot scale testing, economic evaluation and assessment of potential environmental impacts (Mpinga et al., 2018b).

I.7. OVERALL CONCLUSIONS

This investigation has given us a fresh perspective to successfully treat refractory PGM minerals such as sperrylite (PtAs_2), cooperite (PtS), platarsite Pt(As,S)_2 and other lesser-known platinum minerals. Sperrylite consists mainly of platinum chemically combined with arsenic (Mertie, 1969), which is known to form stable high-temperature phases with platinum (Bai et al., 2017; Olivotos and Economou-Eliopoulos, 2016).

A similar observation was made by Mountain and Wood (1988) that, the solubility of PtAs_2 is considerably less than that of Pt metal in hydrothermal solutions. Therefore,

its dissolution efficiency for platinum recovery might only be improved by thermal pretreatment processes supposed to influence the oxidation state of arsenic in the sulfide melt.

I.8. RECOMMENDATIONS AND FUTURE RESEARCH OPPORTUNITIES

This work is by no means an exhaustive study, to make the research scientifically more rigorous, a number of issues need to be addressed in future work. These are:

1. Locked cycle testing and the impact of recycle streams.
2. Studying the fate of residual reagents and wastes.
3. Material balancing the conceptual process.
4. Analyzing the proposed process for hazards and operability.
5. Looking into reagent and heat recovery.
6. Piloting the process in a mini pilot plant.

A further intent is the combined use of Sn(II) and SCN(I) in an attempt to overcome the shortcomings of current commercially available strong-base anion exchange resins presenting prompt PGM loading rates, high loading capacities (of more than 1.5 meq/g as in this investigation) but poor selectivity and elution properties. In addition, the exploration of amphoteric ion exchangers could also be worth revisiting for future projects.

I.9. REFERENCES

Assis, S., Montenegro, L., Peres, A., 1996. Utilisation of hydroxamates in minerals froth flotation. *Minerals Engineering* 9(1), 103-114.

Bax, A., Dunn, G.M., Lewins, D., 2009. Recovery of platinum group metals. USA patent 7544231 B2.

Becker, M., Wiese, J., Ramonotsi, M., 2014. Investigation into the mineralogy and flotation performance of oxidised PGM ore. *Minerals Engineering* 65, 24-32.

Bulatovic, S., 2003. Evaluation of alternative reagent schemes for the flotation of platinum group minerals from various ores. *Minerals Engineering* 16(10), 931-939.

Evans, D.M., 2002. Potential for bulk mining of oxidized platinum-group element deposits. *Applied Earth Science* 111(1), 81-86.

Green, B.R., Smit, D.M.C., Maumela, H., Coetzer, G., 2004. Leaching and recovery of platinum group metals from UG-2 concentrates. *Journal of the South African Institute of Mining and Metallurgy* 104(6), 323-331.

Kalichini, M., Corin, K.C., O'Connor, C.T., Simukanga, S., 2017. The role of pulp potential and the sulphidization technique in the recovery of sulphide and oxide copper minerals from a complex ore. *Journal of the Southern African Institute of Mining and Metallurgy* 117(8), 803-810.

Kraemer, D., Junge, M., Bau, M., 2017. Oxidized Ores as Future Resource for Platinum Group Metals: Current State of Research. *Chemie Ingenieur Technik* 89(1-2), 53-63.

Kraemer, D., Junge, M., Oberthür, T., Bau, M., 2015. Improving recoveries of platinum and palladium from oxidized Platinum-Group Element ores of the Great Dyke, Zimbabwe, using the biogenic siderophore Desferrioxamine B. *Hydrometallurgy* 152, 169-177.

Kuzugüdenli, Ö.E., Kantar, Ç., 1999. Alternates to gold recovery by cyanide leaching. *Erciyes Üniversitesi Fen Bilimleri Dergisi* 15 (1-2), 119-127.

Lee, J., Nagaraj, D., Coe, J., 1998. Practical aspects of oxide copper recovery with alkyl hydroxamates. *Minerals Engineering* 11(10), 929-939.

Lee, K., Archibald, D., McLean, J., Reuter, M., 2009. Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Minerals Engineering* 22(4), 395-401.

Lewins, J., Greeaway, T., 2004. The Panton platinum-palladium project. *The Australian Institute of Mining and Metallurgy Bulletin* July-August 04.

Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012a. Thiocyanate hydrometallurgy for the recovery of gold. Part I: Chemical and thermodynamic considerations. *Hydrometallurgy* 113-114, 1-9.

Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012b. Thiocyanate hydrometallurgy for the recovery of gold Part III: Thiocyanate stability. *Hydrometallurgy* 113-114, 19-24.

Liddell, K.S., Adams, M.D., 2012. Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates. *Journal of the Southern African Institute of Mining and Metallurgy* 112(1), 31-36.

Luszczkiewicz, A., Chmielewski, T., 2008. Acid treatment of copper sulfide middlings and rougher concentrates in the flotation circuit of carbonate ores. *International Journal of Mineral Processing* 88(1), 45-52.

Mpinga, C.N., Eksteen J.J., Aldrich, C., Dyer, L., 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review. *Minerals Engineering* 78, 93-113.

Mpinga, C.N., Eksteen, J.J., Aldrich C., Dyer, L., 2018a. Atmospheric leach process of high-chromitite PGM-bearing oxidized mineralized ore through a single-stage and two-stage techniques. *Minerals Engineering* 125, 165-175.

Mpinga, C.N., Eksteen, J.J., Aldrich C., Dyer, L., 2018b. A conceptual hybrid process flowsheet for platinum group metals (PGMs) recovery from a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization through a single-stage leach and adsorption onto ion exchange resin. *Hydrometallurgy* 178, 88-96.

Mpinga, C.N., Eksteen, J.J., Aldrich, C., Dyer, L., 2017. Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore. *Minerals Engineering* 110, 153-165.

Muir, D.M., Ariti, J., 1991. Studies on the dissolution of platinum and palladium from low grade ores and by-products. In 5th AusIMM Extractive Metallurgy Conference, Perth, Australia (2-4 Oct., 1991), 183-186.

Mwase, J.M., Petersen, J., 2017. Characterizing the leaching of sperrylite (PtAs₂) in cyanide based solutions. *Hydrometallurgy* 172, 1-10.

Mwase, J.M., Petersen, J., Eksteen, J.J., 2012a. Assessing a two-stage heap leaching process for Platreef flotation concentrate. *Hydrometallurgy* 129-130, 74-81.

Mwase, J.M., Petersen, J., Eksteen, J.J., 2012b. A conceptual flowsheet for heap leaching of platinum group metals (PGMs) from a low-grade ore concentrate. *Hydrometallurgy* 111-112, 129-135.

Mwase, J.M., Petersen, J., Eksteen, J.J., 2014. A novel sequential heap leach process for treating crushed Platreef ore. *Hydrometallurgy* 141, 97-104.

Newell, A., Bradshaw, D., Harris, P., 2006. The effect of heavy oxidation upon flotation and potential remedies for Merensky type sulfides. *Minerals Engineering* 19(6), 675-686.

Oberthür, T., Melcher, F., Buchholz, P., Locmelis, M., 2013. The oxidized ores of the main sulphide zone, Great Dyke, Zimbabwe: turning resources into minable reserves-mineralogy is the key. *Journal of the Southern African Institute of Mining and Metallurgy* 113(3), 191-201.

Oberthür, T., Melcher, F., Buchholz, P., Locmelis, M., 2013. The oxidized ores of the main sulphide zone, Great Dyke, Zimbabwe: turning resources into minable reserves-mineralogy is the key. *Journal of the Southern African Institute of Mining and Metallurgy* 113(3), 191-201.

Okamoto, H., 1990. The As-Pt (Arsenic-Platinum) system. *Journal of Phase Equilibria* 11(5), 508-510.

Sefako, R., Sekgarametso, K., Sibanda, V., 2017. Potential Processing Routes for Recovery of Platinum Group Metals from Southern African Oxidized PGM Ores: A Review. *Journal of Sustainable Metallurgy* 3(4), 797-807.

Shaik, K., Petersen, J., 2017. An investigation of the leaching of Pt and Pd from cooperite, sperrylite and column bioleached concentrates in thiocyanate-cyanide systems. *Hydrometallurgy* 173, 210-217.

Sole, K.C., Feather, A.M., Cole, P.M., 2005. Solvent extraction in southern Africa: An update of some recent hydrometallurgical developments. *Hydrometallurgy* 78(1), 52-78.

Tatarnikov, A.V., Sokolskaya, I., Shneerson, Y.M., Lapin, A.Y., Goncharov, P.M., 2004. Treatment of platinum flotation products. *Platinum Metals Review* 48(3), 125-132.

Wan, R.Y., LeVier, K.M., 2011. Precious metal recovery using thiocyanate lixiviant. US Patent 7947108 B2.

CHAPTER II : LITERATURE REVIEW

Submitted for publication as

Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review.

C.N. Mpinga, J.J. Eksteen, C. Aldrich, L. Dyer., 2015.
Minerals Engineering 78, 93-113.

Accepted for publication on 10th April 2015.

© 2015 Elsevier Ltd.

Reprinted with permission from the publisher.

SUMMARY

This Chapter provides an overview of the most recent and relevant academic studies on the topic under discussion, as well as an evaluation of theory related to the subject. The perceived knowledge gaps paved a way to the current research.



Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review



C.N. Mpinga, J.J. Eksteen*, C. Aldrich, L. Dyer

Department of Mining Engineering and Metallurgical Engineering, Western Australian School of Mines, Curtin University, GPO Box U1987, Perth 6845, Western Australia, Australia

ARTICLE INFO

Article history:

Received 8 December 2014

Revised 8 April 2015

Accepted 10 April 2015

Available online 16 May 2015

Keywords:

Low-grade deposits

Refractory materials

Platinum group metals

Platinum and palladium recovery

Leaching

ABSTRACT

Platinum Group Metals (PGMs), often with associated gold, have very few occurrences where they are present in an ore deposit at economically extractable levels. They are classified as both precious and critical metals due to their scarcity and their wide industrial use. With deteriorating socio-political environments in most primary PGM producing countries, PGM deposits that are smaller but in less risky jurisdictions have to be evaluated. However, the lower PGM grades, increased mineralogical complexity of the ores, capital intensity and strict environmental regulations in other international jurisdictions, limit the implementation of conventional metallurgical processing options, particularly smelter-based operations. The conventional smelter-based process options are justifiable for high grade, low chromite, large resource and long life-of-mine operations.

In the present paper, we review some of the most recent literature on the predominantly hydrometallurgical approaches to PGM extraction. A number of metallurgical processes that generate either a PGM rich leachate or a residue containing metal values, and the various methods in use for their recoveries from pregnant rich solutions are reviewed. Sixteen process flowsheet variants combining conventional and proprietary unit process technologies are provided, and their process chemistries and key technical operating parameters are compared. Where appropriate, the key thermodynamic and kinetic factors are given and compared.

© 2015 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	94
2. Remote PGM deposits in friendly jurisdictions: A Western Australian example	94
3. Existing technologies in the extractive metallurgy of low-grade refractory precious metals	96
3.1. Precious metal rich solution processes	96
3.1.1. Chloride-based atmospheric leach process: Intec Copper process	96
3.1.2. Sulfate-based pressure leach process: Platsol® process	97
3.2. Precious metal rich residue processes	98
3.2.1. Cyanide-based atmospheric leaching	98
3.2.2. Cyanide-based pressure leaching: Two-stage selective pressure leach process	99
3.2.3. Chloride-based processes	100
3.2.4. Sulfate-based leach processes	101
3.2.5. Galvanically-assisted chalcopryrite leach process: Galvanox™	105
3.3. Summary	106
4. Use of unconventional lixiviants	106
4.1. Alkaline glycine leach processes	106
4.2. Halide system (bromide, chloride and iodide) leach processes	106
4.2.1. Iodide leach processes of precious metals	107
4.2.2. Chloride leach processes of precious metals	107

* Corresponding author.

E-mail address: jacques.eksteen@curtin.edu.au (J.J. Eksteen).

4.2.3.	Bromide leach processes of precious metals	107
4.3.	Thiosystem (thiosulfate, thiocyanate and thiourea) leach processes	108
4.3.1.	Thiourea leach processes of precious metals	108
4.3.2.	Thiosulfate leach processes of precious metals	108
4.3.3.	Thiocyanate leach processes of precious metals	108
5.	Conclusions	110
	Acknowledgements	111
	References	111

1. Introduction

The members of the Platinum Group Metals (PGMs) [platinum (Pt), palladium (Pd), iridium (Ir), osmium (Os), rhodium (Rh), ruthenium (Ru)] plus gold (Au) are called “precious” metals (PMs). Platinum, palladium and gold are of major commercial significance. Rhodium is the next most important, while iridium and ruthenium are traded in moderate quantities. Osmium is rarely used (Fact Sheet, 2012; Harjanto et al., 2006). The PGMs have very high melting points, are chemically inert to a wide variety of substances (even at very high temperatures), and thus resist corrosion. They also have excellent catalytic properties, and are widely used in the chemical industry and in automobile catalytic converters (Afolabi et al., 2012). According to figures published by Mieziitis (2014), gross demand for platinum and palladium fell marginally in 2012 to 8.05 and 9.90 Moz, respectively. Over the last five years, between 72% and 77% of total annual platinum supply has come from primary mining output, the rest being originated from the recycling (WPIC, 2014). The amounts and principal locations from which PGMs have been mined as a primary product and/or recovered as a by-product of base-metal mining from 1995 through 2010 are shown in Fig. 1.

The major portion of platinum and palladium produced today from primary sources originates from the Bushveld Igneous Complex in South Africa. The most important reefs mined are the Merensky, Upper Group Two (UG-2) and Platreef (Cramer, 2001). Ore grades range from 3 to 8 g/t PGM, with associated nickel and copper in the 0.1–0.2% range present mainly as sulfides (Kyriakakis, 2005). South Africa dominates the PGMs world production followed by Russia with minor contributions from Canada, Zimbabwe, the USA and Colombia. South Africa, Russia and Canada have approximately 98% of the known global PGM reserves.

Platinum group metals are conventionally recovered from high-grade concentrates (typically assay of 200 to over 2000 g/t PGM with 0.4–2.8% Cr₂O₃) by the traditional matte-smelting-refining technique depicted in Fig. 2 (Cole and Joe Ferron, 2002). Ore is first ground by conventional multistage crushing and ball milling, or by semi-autogenous grinding (SAG), and then smelted. The matte is hydrometallurgically treated to leach and separate Fe, Co, Ni and Cu leaving a slime containing 10–50% of precious metals (Chen and Huang, 2006). Note that flotation of conventional chromite rich ores is usually done in a mill-float-mill-float (MF2) open circuit, to prevent the accumulation of chromite fines derived from overgrinding in recirculating loads.

Just to mention a few, sizeable PGM resources with more chromite challenging mineralogies have been identified in Finland and Australia (Wilburn, 2012). The Penikat and Portimo intrusions in northern Finland have generated the most interest (Gold Field's Arctic Platinum project or Suhanko). Suhanko can be described as palladium/platinum deposits (average ratio of approximately 4–1) with some significant base-metal by-products (Wilburn and Bleiwas, 2004). Total mineral resources in the Arctic Platinum Project, including the SK Reef, currently stand at 168.3

million tons containing 12.60 million ounces (Pt + Pd + Au) at a grade of 2.33 g/t, and include 330,000 tons of copper and 140,000 tons of nickel (Saari, 2005). The three major Australian PGM deposits (i.e., Munnii Munnii, Panton and Fifield) contain a total of 100,460 kg PGM, which captures at least 80–90% of Australia's known resources (Koek et al., 2010). Fig. 3 shows various PGM projects in “friendly” (i.e. low socio-political risk) mining jurisdictions with their resource size and PGM grade (Trickey, 2010). It is quite clear that most deposits are fairly small (less than 100 million tons of ore, with intermediate (1 g/t < grade < 5 g/t) grades. It highlights that most of the resources in friendly mining jurisdiction do not have the resource base to warrant a smelter complex.

The features that these deposits (Finnish and Australian) tend to have in common are that they are characterized by relatively high Cr content (Lewins, 2006; Saari, 2005). However, with high chrome levels of more than 2.8%, pyrometallurgical processes are not attractive on account of the build-up of highly refractory chromite spinel layers in the furnace. In addition, the combination of high chromite, high talc and fineness of grind of PGM concentrates have led to dangerously high matte temperatures (Eksteen, 2011; Eksteen et al., 2011; Ritchie and Eksteen, 2011). Another major problem with smelting is the environmental costs due to the high pollution level from this traditional technology as environmental standards continue to stiffen, particularly regarding toxic wastes such those with cyanide compounds.

A few of these new projects outside Southern Africa (see Fig. 4) may contribute to further growth in platinum industry. In the present paper, we review some of the most recent literature on the topic, with a view to providing the full scope of developments in the field.

2. Remote PGM deposits in friendly jurisdictions: A Western Australian example

According to Mieziitis (2014), the total identified PGM resources in Australia are about 276,000 kg (shallow deposit). Of this amount, deposits that have only PGM resources account for about 51%. Australia's annual platinum and palladium production equates to less than 0.2% of global supply (about 700 kg a year) with all production being a by-product of mining nickel sulfide deposits in the Yilgarn Craton in Western Australia. Australia remains poorly explored with regard to PGMs. No resource is being exploited for PGMs as the main (economic) product. Australia can make a larger contribution if it can find ways to economically exploit its smaller stranded deposits.

PGM ore from the Panton Sill deposit, a Bushveld-type deposit in the Kimberly region of Western Australia, contains 2.19 g/t Pt, 2.39 g/t Pd associated with 0.31 g/t Au, 0.27% Ni, and 0.07% Cu – providing sufficient tonnage: design capacity of 1500 kg/year of recoverable PGMs – is currently being evaluated for precious metals recovery. The PGMs occur as discrete phases with most grain diameters in the 3–11 μm range, typically at particle boundaries or as locked inclusions hosted by silicates, carbonates

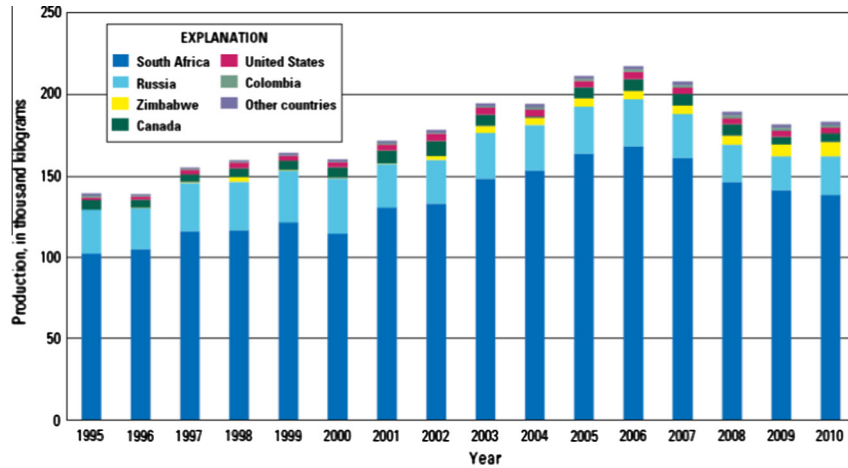


Fig. 1. Worldwide PGMs production as primary product and/or recovered as a by-product of base-metal mining from 1995 through 2010 (Wilburn, 2012).

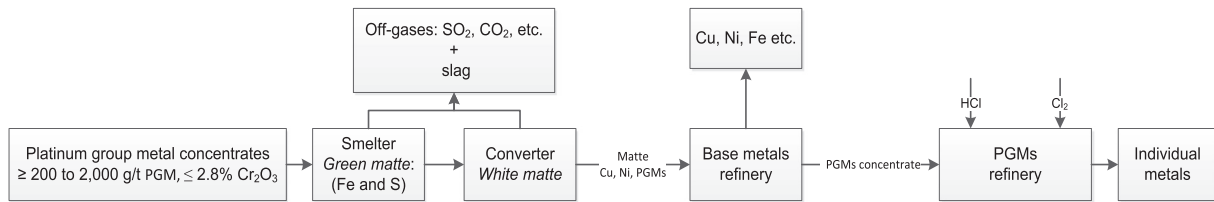


Fig. 2. Conventional PGM concentrate matte-smelting-refining technology.

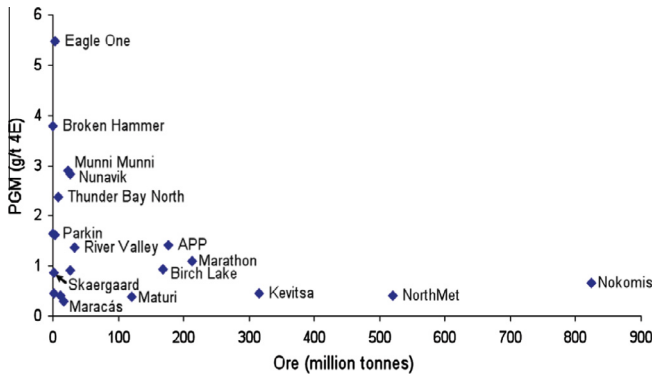


Fig. 3. Comparison of project resource size and PGM grade (Trickey, 2010).

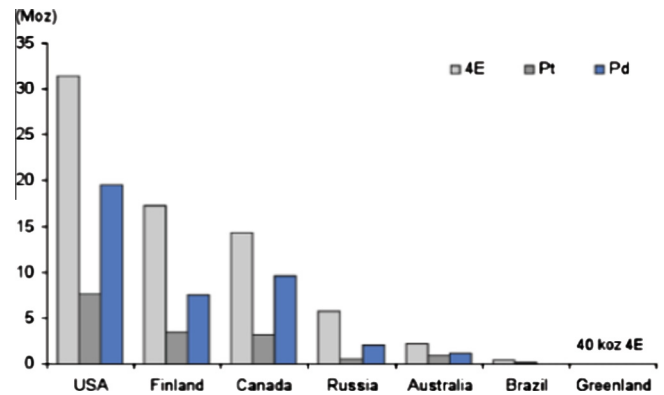


Fig. 4. Distribution of PGM project resources outside of Africa (Trickey, 2010).

and chromitites. The main palladium phase is palladium antimonide while sperrylite (platinum di-arsenide) is the main platinum phase. The predominant base metal sulfides were identified (Lewins and Greenaway, 2004) as pentlandite, chalcopyrite and pyrite.

The fine grained nature of the PGMs and the presence of significant soft, fine grained altered silicates leads to a high flotation mass pull (i.e. concentrate to ore ratio) requirement in order to achieve acceptable PGM grade recoveries. This in turn, results in grade dilution and poor quality concentrates which cannot be economically processed by PGM smelters, in addition to large transport costs should concentrate transport be considered. The resource is not sufficiently large to justify the building of a smelter at site, and the area is very poorly serviced with power and water infrastructure.

Panton flotation recoveries of about 65% into a final concentrate of around 100 g/t PGM combined with high chrome levels of more than 5% means that the product is unattractive to smelters (Lewins,

2006). The ratio of PGMs to each other being palladium rather than platinum rich (compared to South African and Zimbabwean ores) implies a lower income than for a Southern African ore of similar total PGMs. Note that for South African producers, the approximate distribution of the operating costs for each stage is as follows: 72% mining, 10% concentrating, 9% smelting and 9% refining (Jones, 2005).

Due to its (concentrate) relatively low sulfur content, and because the resource is too far away from a market, sulfuric acid manufacture tends to be uneconomic. Conversely, the sulfur content is still sufficiently high to cause significant environmental impact and therefore, has to be scrubbed using fairly expensive flue gas desulfurisation technologies such as dual alkaline scrubbing technology to produce a mixture of CaSO_3 and CaSO_4 (Bezuidenhout et al., 2012; Eksteen et al., 2011). This adds significant capital and operating costs to smelting of chromite-rich PGM concentrates.

The concentrate smelt–refine route results in approximately 144 kg CO₂ equivalents, 0.45 kg SO₂ and consumes roughly 753 m³ of water per ton of ore milled (Anglo American, 2011). Furthermore, the lengthy overall flowsheet results in unavoidable PGM losses (Chen and Huang, 2006). Jones (2005) argued that PGMs recovery is typically about 85% in the concentration stage, 95–98% in smelting and 99% in refining. An alternative process to recover PGMs has been proposed by other researchers where PGMs are leached into an aqueous cyanide solution, in which they are solubilized as precious metal–cyanide complexes (Mwase et al., 2014; Chen and Huang, 2006; Aguilar et al., 1997; Trexler et al., 1990).

Cyanidation has been the predominant process for gold recovery from mineral resources for more than a century because of its simplicity and economy (Deschenes, 2005; Staunton, 2005; Holtum and Murray, 1994; McInnes et al., 1994). In some instances – the case for many oxide ores – gold and silver are leached directly from ores/concentrates (Prasad et al., 1991). In other occurrences, such as precious metals bearing sulfide ores, the ores are often too refractory to direct cyanide leaching even after fine grinding. The refractoriness of precious metal ores/concentrates to conventional cyanide leaching can be related to carbonaceous materials presence (preg-robbing activity), precious metals association with sulfide minerals, and silica encapsulation (Senanayake, 2004a; Wan et al., 1993).

In such cases, it is essential to pre-treat the ore/concentrate by roasting, pressure oxidation, bio- or chemical oxidation, or mechanical activation to degrade carbonaceous materials or oxidize sulfide materials (Ellis et al., 2008; Senanayake, 2004b; Prasad et al., 1991). The precious metals are thereby released for recovery during subsequent cyanide leaching whilst destroying potential cyanicides such as base metal sulfides (Wan and LeVier, 2011; Lorenzen and van Deventer, 1992; Afenya, 1991).

Many recent research and development activities have focussed on precious metals extraction from refractory low-grade ore/concentrate using predominantly hydrometallurgical technologies due to increasing industrial need for these metals, the cost and infrastructure requirements associated with smelting, the smaller resource sizes outside of South Africa and Russia, and their limited sources (Liddell and Adams, 2012; Dreisinger, 2012; Chen and Huang, 2006). The Polokwane smelter (in South Africa) is one of the most recently installed and has been designed to accommodate a higher UG-2 content with 4% Cr₂O₃ in the feed, throughput of 650,000 tonnes per year at 85% availability (87 t/h) (Liddell et al., 2010).

As in the processing of copper–gold and refractory sulfide hosted gold ores, where the base metals and sulfur have to be removed to expose the precious metals for extraction and to limit reagent consumption, PGMs have to be made accessible to interact with the lixiviant by removing the Cu and Ni sulfides (chalcopyrite and pentlandite); and converting iron sulfides (pyrrhotite and pyrite) into a form that does not lock up PGMs. These base metal removal technologies are reviewed below.

3. Existing technologies in the extractive metallurgy of low-grade refractory precious metals

There are many publications reviewing copper and/or nickel hydrometallurgy or the combination pyro-hydrometallurgy processes as a pre-treatment step toward PGM recovery from ores/concentrates (Li et al., 2013; Li and Miller, 2006; Wang, 2005; Xiao and Laplante, 2004; Fleming, 2002; Maurice and Hawk, 1999; La Brooy et al., 1994). However, the exact chalcopyrite leaching mechanism is not proven, the final flowsheet (universal process) for its treatment from ores/concentrates is still not

determined. To date chalcopyrite leaching has not been widely adopted by industry due to its extremely slow leach kinetics (Li et al., 2013).

Many authors have suggested that the leaching process is inhibited by the formation of a passivating layer that does not allow further reaction to occur, but there is no scientific consensus on the actual layer composition neither on its formation mechanism (Li et al., 2013; Mateos et al., 1987). Three possible causes for this phenomenon have been identified: (1) adherent film formation of sulfur (S⁰), disulfide (S₂²⁻) and/or polysulfide (S_n²⁻) on the mineral particle surface, which reduces the diffusion of the leaching agent to the mineral reacting surface, (2) the formation of a copper rich polysulfide layer developed on the surface as a result of solid state changes that occur in the mineral during leaching and (3) formation of impermeable layer comprised of Fe hydroxy-oxide compounds (Debernardi et al., 2013; Li et al., 2013; Nazari and Asselin, 2009).

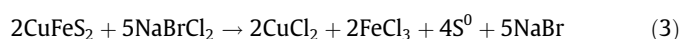
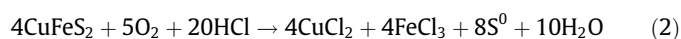
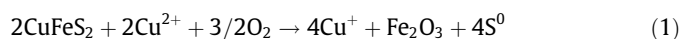
Therefore discussion in the present section will be mainly limited to chalcopyrite ores/concentrates treatment, since chalcopyrite is both one of the precious metals hosting minerals and the most difficult to leach (refractory). Thereby any chalcopyrite successful process will be hopefully capable of treating pentlandite which is also refractory (Maurice and Hawk, 1999). In the following sections, processes are grouped according to whether or not PGMs and/or gold are (is) leached into solution at first solid–lixiviant contact (single step leaching) or remain concentrated in the insoluble leach residue, calcine/roaster products following the pre-oxidation step until further hydrometallurgical treatment.

3.1. Precious metal rich solution processes

Hydrometallurgical treatments – generally have greater flexibility during the process scale and control – are making inroads into the field traditionally dominated by smelting and refining. Milbourne et al. (2003) stated that a direct hydrometallurgical treatment route from flotation concentrate to refinery feed is desired by the industry to provide the benefits of reduced treatment charges, lower working capital, and better metal winning economy at mine-site scale, as well as greater marketing flexibility for the product.

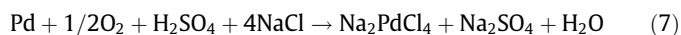
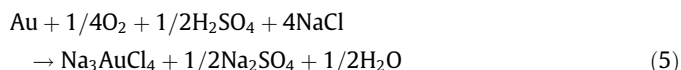
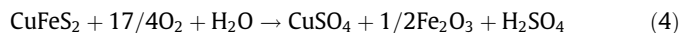
3.1.1. Chloride-based atmospheric leach process: Intec Copper process

The Intec Copper process is a proven, patented hydrometallurgical technology for copper and precious metals extraction from sulfide concentrates (Moyes and Crescent, 1999). The process involves multistage leaching (in countercurrent configuration) and uses a strong mixed chloride–bromide lixiviant (280 g/L NaCl and 28 g/L NaBr), where chalcopyrite is leached by cupric ions and air at atmospheric pressure and temperatures below 100 °C (typically 85 °C) forming a solution of cuprous ions. At the same time, sulfide and iron are rejected into the leach residue as elemental sulfur and hematite (Eqs. (1)–(3)) rather than an unstable jarosite (Palmer and Johnson, 2005; Sammut and Welham, 2002). The main basic approaches of the process are depicted in Fig. 5.



Intec process removes copper minerals (cyanicides) prior to cyanidation-CIP/CIL. However, sulfur is renowned for passivating precious metals surfaces, leading to poor subsequent leach recoveries (Li et al., 2013; Nazari et al., 2011; Pugaev et al., 2011; Córdoba et al., 2008). Then sulfur reacts with cyanide to form

in the reactions in Eqs. (4)–(7) (Dreisinger, 2012; Fleming, 2002). The PGMs and gold are then recovered from the pregnant rich solution using either sulfide precipitation, activated carbon adsorption, or ion exchange (Liddell and Adams, 2012).



The Platsol[®] process is a variant of the high temperature Total Pressure Oxidation (TPOX) discussed later in Section 3.2.4, point B. The fundamental difference between the two processes is the chloride ions addition in sulfuric medium to the autoclave feed in the Platsol[®] process (Fleming, 2002). Liddell and Adams (2012) pointed out that the Platsol[®] process disadvantages include potential incomplete PGM leach recoveries from more refractory mineral phases and carry-over losses of precious and base metals at the metals separation and recovery stages, due to co-precipitation and adsorption effects. The majority of iron present in the concentrate is rejected into the residue, thereby effecting the solid–liquid separation (Milbourne et al., 2003). In addition, with the Platsol[®] process, it is difficult to optimize the conditions independently for each value metal species, to maximize their dissolution and recovery.

Ferron et al. (2006) have observed that most PGMs and their minerals were amenable to the Platsol[®] process with the notable exception of cooperite (PtS). Cooperite is generally known to be more refractory than sperrylite (PtAs₂) minerals (Adams et al., 2011). Ferron et al. (2006) also observed that concentrates amenable to the Platsol[®] process are those containing high sulfide and iron values. Platsol[®] leaching technology on Panton concentrates, from Platinum Australia Limited, recorded 95% PGM dissolution but with unacceptably high reagent consumption presumably caused by co-leaching of other feed constituents (Lewins and Greenaway, 2004). The effective Panton concentrates leaching may be attributed to the presence of native metals and metal alloys such as Pt–Fe, Pd–Cu–Fe, Pt–Pd–Fe, Pt–Fe–Ni and Pd–Pb along with other PGM sulfides, antimonides, bismuth, etc.

Similar technology used at Mintek (Green et al., 2004), in an attempt of recovering Pd (23 g/t) from a material derived from a sulfidic ore, gave recoveries between 40% and 50%. The authors concluded that successful leaching requires satisfactory PGM grain liberation and refractory minerals conversion (sulfides, arsenides, etc.) to native metals, alloys or amenable compounds. The technology did not decompose PGM sulfides. In the Platinum Australia Limited's work, it is assumed that PGM minerals were well liberated (less refractory) based on the high recoveries observed. Finally, according to Dreisinger (2006), Platsol[®] technology is under final feasibility study for application by PolyMet Mining at the NorthMet deposit in Minnesota, USA. Gold Fields Ltd. has

evaluated Platsol[®] in their prefeasibility study for their Arctic Platinum division consisting of the Suhanko, Narkaus and Penikat projects (Gold Fields, 2013).

3.2. Precious metal rich residue processes

The precious metals are either concentrated in the insoluble sulfuric acid first campaign leach residue, calcine or roaster products following the pre-oxidation step. Hence the solid residue is the primary precious metals concentrate for further hydrometallurgical treatment.

3.2.1. Cyanide-based atmospheric leaching

3.2.1.1. *Sequential heap leach process.* A low-cost hydrometallurgical process depicted in Fig. 7, an alternative to smelting, consisting of a heap bioleach process to first extract the base metals (BMs); followed by a caustic rinse of the residue material and a heap cyanidation process to subsequently extract the PGMs, has been suggested for treating low-grade ores/concentrates (Mwase et al., 2014, 2012a,b). Lonmin Plc has also developed and patented a novel integrated hydrometallurgical method suitable to treat efficiently and economically low-grade PGM sulfide concentrates with large amounts of chromite gangue (Bax et al., 2009).

A problem with this approach is that the residual solids following oxidative pre-treatment are frequently highly acidic, while the cyanide leach process should be conducted at an alkaline solution pH of more than 9.31, the optimum being 10.3 (Heinen et al., 1978). It is often advantageous to work at solution pH above the HCN pK_a value of 9.31 in order to prevent the formation of HCN and its possible release, and pH > 9.3 ensures that most of the cyanide is in its ionic form (Fleming, 1992). As a consequence, it is necessary to neutralize the solids prior to cyanide leaching (Mwase et al., 2012a,b). This neutralization typically requires adding large quantities of alkali to the solids, significantly adding to the expense and complexity of the operation such as material handling (Wan and LeVier, 2011; Senanayake, 2004b).

Investigative experimental work by Platinum Australia Limited (PLA) on Panton concentrates (P₈₀ of 38 μm) showed that atmospheric cyanide leaching could recover up to 86% Pd, 99% Au, but less than 10% Pt. Fine grinding to P₈₀ of 14 μm provided only small improvement. It can be speculated that the low leaching temperature might have contributed. Green et al. (2004) recorded less than 25% PGMs recovery while leaching UG-2 flotation concentrate, presumably because only 30% of PGM grains were liberated and 60% were associated with base metal sulfides, mainly pentlandite and chalcopyrite, either on edges or locked into base metals. No single industrial operation using the current sequential heap leach strategy has been reported.

3.2.1.2. *Panton process.* Platinum Australia Limited (PLA) in conjunction with Lonmin Plc have developed the Panton process, in which low-grade flotation concentrates are subjected to low-temperature calcination followed by cyanide leaching at elevated temperature to dissolve the PGMs, gold and base metals as per the

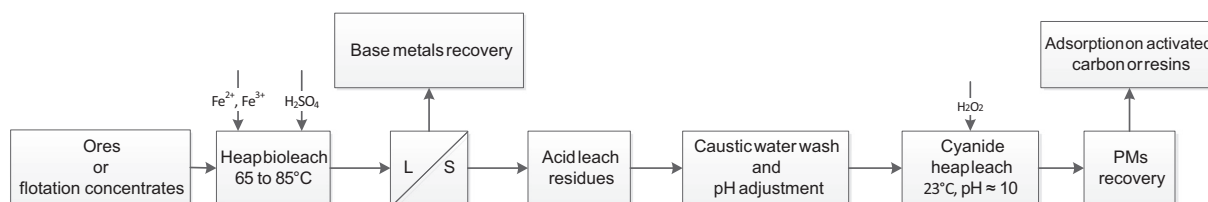


Fig. 7. Sequential heap leach process for base and precious metals recovery.

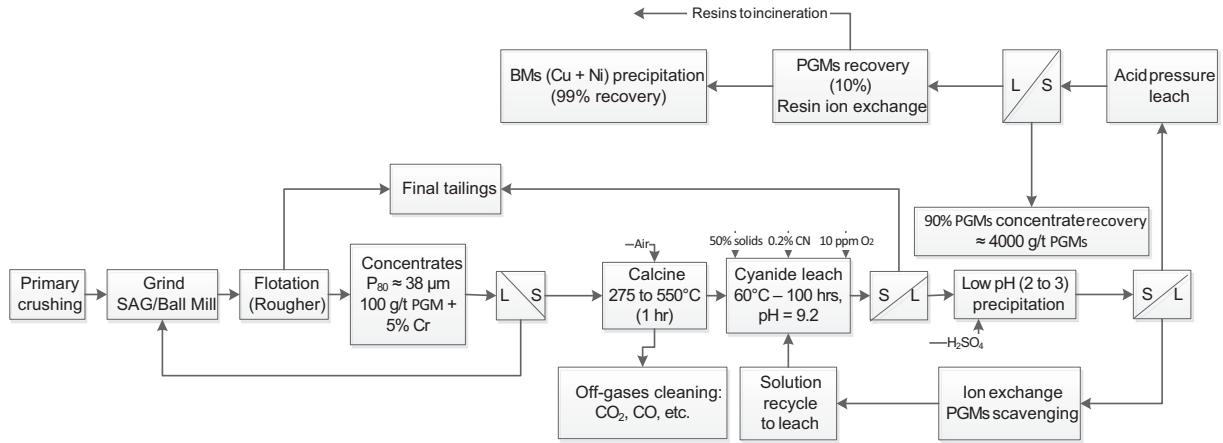


Fig. 8. Panton process conceptual flow schematic (Lewins and Greenaway, 2004).

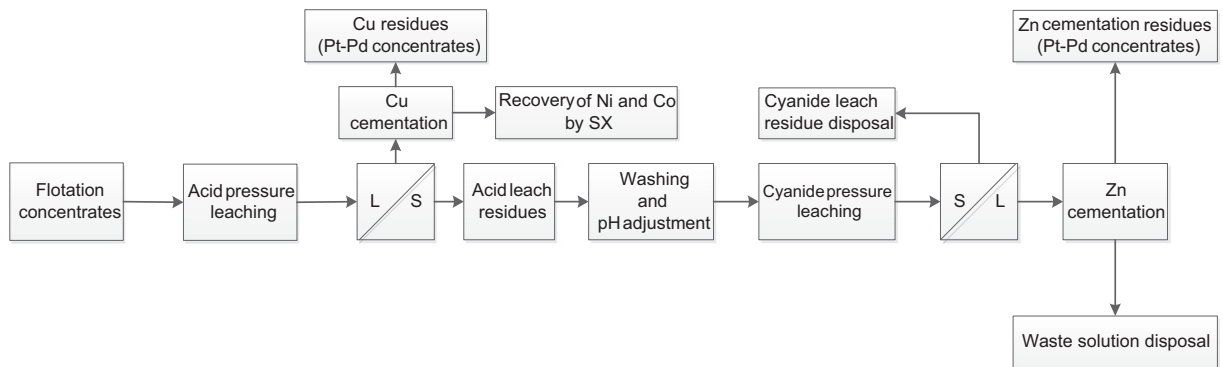


Fig. 9. Two-stage selective pressure leaching for Pt-Pd flotation concentrates treatment.

simplified flowsheet presented in Fig. 8 (Snyders et al., 2012, 2013; Lewins and Greenaway, 2004). Cyanide dissolved base and precious metals are recovered from the pregnant solution by precipitation to produce high-grade base and precious metal concentrates suitable as direct feed to refineries (Bax, 2004).

On Panton Sill concentrates, the process recorded significantly higher recoveries of 90.8% Pt, 91.9% Pd, 94.4% Au, 69% Cu and 32% Ni (Lewins and Greenaway, 2004). Although roasting is viable at relatively low temperatures of 275–550 °C, it requires high capital expenditure to ensure good heat recovery. Furthermore, Sanders (1926) has argued that roasting or smelting PtAs₂ to temperatures of 450 °C or more, arsenic turns from its solid into the gaseous state thereby inducing platinum to do likewise, hence escape into the atmosphere as a total loss. Finally, the growing concern with environmental protection increases the restriction on building new cyanide plants. No single industrial operation using the Panton process has been reported.

3.2.2. Cyanide-based pressure leaching: Two-stage selective pressure leach process

Huang et al. (2006) stated that the two-step hydrometallurgical process depicted in Fig. 9 was able to handle concentrates containing low sulfur and high MgO. It is worth mentioning two case scenarios: (1) in acidic pressure leaching, MgO neutralizes the released acid from sulfide oxidation, reducing the leach solution acidity and allowing the flotation plant to produce a high MgO concentrate without a huge rejection of impurity fractions. This in turn maintains high flotation yield, i.e., metal recovery as talc (main source of magnesium) does not have to be suppressed as much during flotation. (2) In case where a pyrometallurgical route is considered, magnesium and chromium have reduced solubility in smelting slags at conventional temperatures due to the formation of magnesium-iron-chromite spinel minerals (Fleming, 2002).

According to the process, precious metals in the iron residue from pressure acid leach can be leached by pressure cyanidation following a caustic wash and solution pH adjustment.

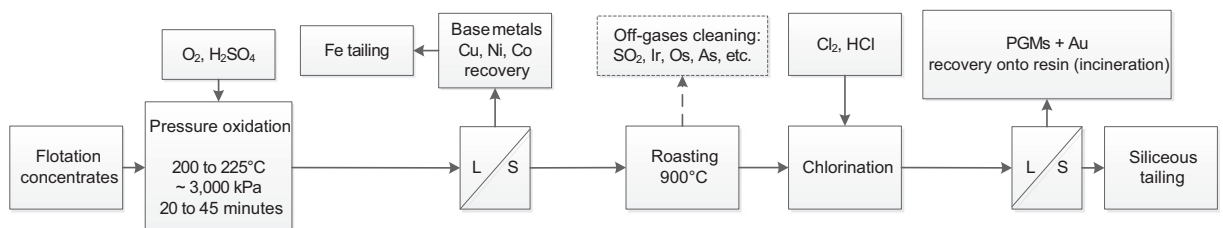


Fig. 10. Simplified block flow diagram of the Kell process.

Investigative work by Platinum Australia Limited (PLA) showed that pressure cyanidation could achieve only 60–69% PGM recovery. Once again, besides this low PGM recovery, there are still increased regulatory restrictions placed on cyanide use for leaching operations due to toxicity and environmental concerns (Aylmore, 2005; Senanayake, 2004a). In order to protect aquatic life species, the Australian Water Quality Guidelines provide a trigger value of 4 µg/L of [CN⁻] (Cyanide management, 2008).

It is pertinent to mention Mwase et al. (2012b) who stated that cyanide is proven to be the most effective and most environmentally acceptable reagent due to the fact that it undergoes natural oxidation converting it to CO₂ and N₂. Note that HCN has a half-life of 267 days after release into the atmosphere (Korte et al., 2000). Furthermore, Mwase et al. (2012b) dealt with cyanide products without differentiating their chemistry, and were thus probably unaware of the interesting observation which Adams et al. (2008) had made a few years earlier, that the presence of copper in tailings supernatant tends to stabilize weak-acid dissociable cyanide in a form toxic to wildlife yet less amenable to natural degradation processes. The Romanian dam disaster, on 30th January 2000 with serious consequences, might be used as an example (Korte et al., 2000). No single industrial operation using the two-stage selective pressure leach process has been reported.

3.2.3. Chloride-based processes

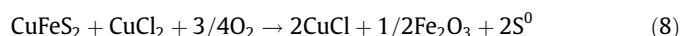
3.2.3.1. Kell process. The Kell process is a patented hydrometallurgical alternative to PGM smelting. This process is a mixed chloride/sulfate based technology, where base metals are removed by sulfuric acid pressure leaching and PGMs are leached after roasting with Cl₂/HCl as commonly used in PGM refining. However, the solution concentrations of PGMs for the Kell process tend to be lower. According to Liddell et al. (2010) and Tatarnikov et al. (2004), the technology is insensitive to the chromite content in the feed. As depicted in Fig. 10, the process comprises three major unit operations including (1) an autoclave for oxidative and selective pressure leaching of base metals and sulfur, (2) a roasting pre-treatment step to render PGMs and particularly Pt amenable to leaching and (3) chlorination of precious metals (Adams et al., 2011). Dissolved precious metals are recovered from the pregnant rich solution by adsorption onto ion exchange resins that are then incinerated to produce a final high-grade PGM concentrate containing 80–85% PGMs plus gold (Liddell and Adams, 2012).

Criticisms of the Kell process are that Cl₂ gas is highly corrosive requiring special materials of construction and therefore results in both high capital and operating costs if such technology is adopted. The same arguments prevail for any chloride-based process. Liddell and Adams (2012) have argued that chlorination leaching has become a standard unit process in PGM refineries. It is pertinent

to mention that the refinery is more the size of a large pilot scale laboratory or a small pharmaceutical plant owing to the low volume of feeds, usually with a monthly tonnage of 4–5 tonnes as compared to the thousands of tonnes of low-grade concentrates to be processed if such technology was adopted (Mwase, 2009). Furthermore, the long-term materials performance is not as well proven. Finally, one of the challenges for all PGM refineries, when evaluating new routes, is the introduction of more contaminants such as S, Se, Te, Bi, Cr, Hg, Si, and Pb. These contaminants are often not sufficiently well evaluated during the process development. The Kell process has not yet been applied commercially. Pilot-scale testing and engineering study work are in progress for several selected sites (Liddell and Adams, 2012).

3.2.3.2. Outokumpu HydroCopper® process. The HydroCopper® process (chloride-based leaching process) developed by Outokumpu Technology in Finland, involves countercurrent leaching of chalcopyrite concentrates using air or oxygen and chlorine as oxidants. Copper sulfide concentrate is leached in a strong NaCl solution. In typical HydroCopper® technology, NaCl concentrations are 230–280 g/L, solution pH can vary between 1.5 and 2.5 and temperature between 80 and 100 °C, at atmospheric pressure (Lundström et al., 2005, 2009; Senanayake, 2009). Generally, chalcopyrite leaching in chloride media, with Cu²⁺ as oxidant, is more effective than in sulfate media with Fe³⁺ as oxidant (Lundström, 2009; Lundström et al., 2007). Cupric ion concentration should be greater than 9 g/L for successful operations (Lundström et al., 2005).

Copper goes into solution as Cu⁺ (Eq. (8)) while iron is precipitated as hematite (Wang, 2005). According to Kowalczyk and Chmielewski (2008), the process is capable of leaching all kinds of copper sulfide concentrates at atmospheric pressure and temperatures of around 80–100 °C using stirred reactors, thickeners and other conventional hydrometallurgical equipment.



In this process, chlorine oxidizes Cu(I) to Cu(II) (Eq. (9)) and copper is recovered from the purified leach solution by precipitating cuprous oxide with caustic soda (Eq. (10)). Then, metallic copper is produced by hydrogen reduction (Eq. (11)). The same process produces and provides (Eq. (12)) all of the chlorine, sodium hydroxide, and hydrogen needed to operate (Wang, 2005). Sulfide sulfur is removed as elemental sulfur, chlorine and hydrogen gases are recycled back to the process (Lundström, 2009). Gold is leached at potentials of >800 mV (vs. SHE) and then recovered from the pregnant solution by precipitating it on activated carbon or copper concentrate. Fig. 11 depicts the general HydroCopper® process flow diagram.

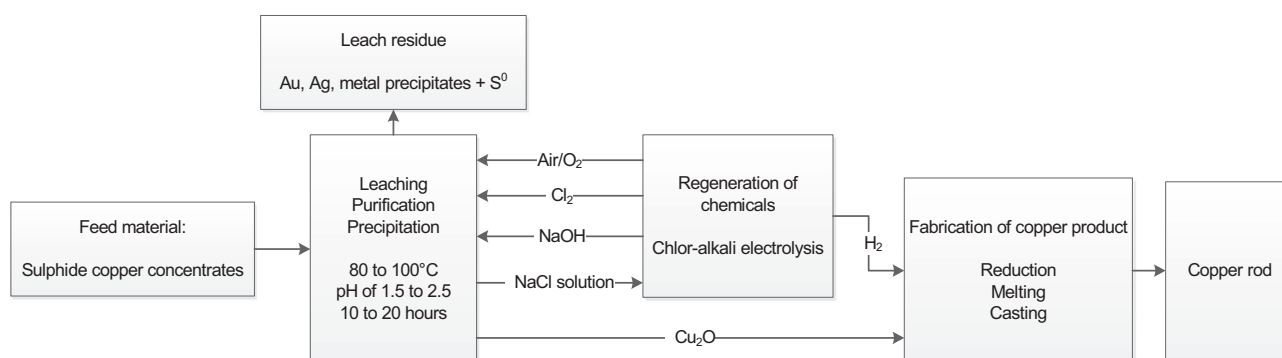


Fig. 11. Outokumpu HydroCopper® process conceptual flow schematic.

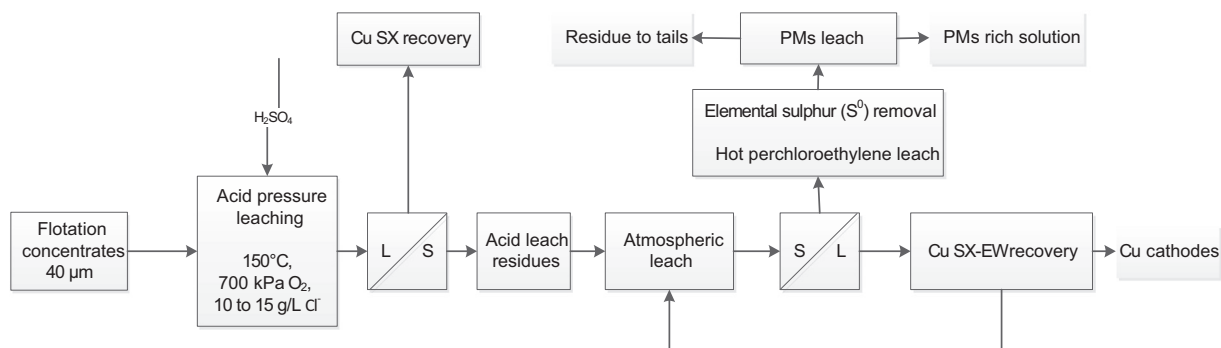


Fig. 12. Simplified CESL process conceptual flow diagram for base and precious metals recovery.

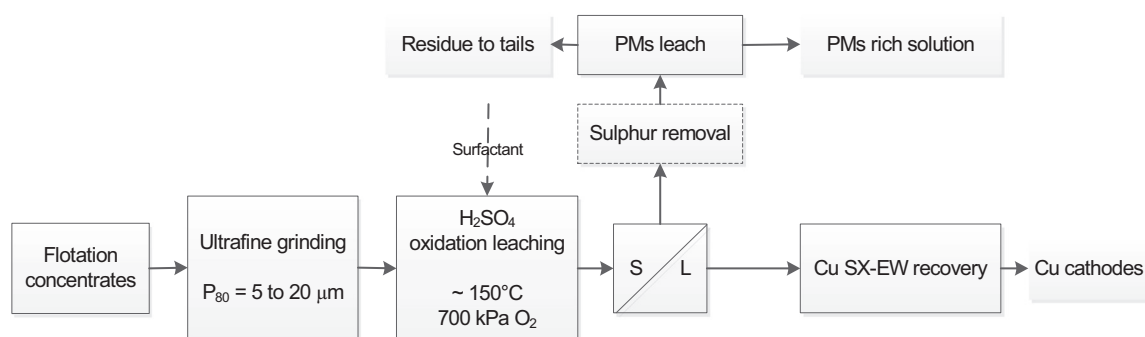
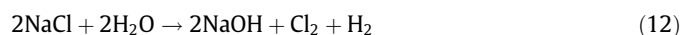
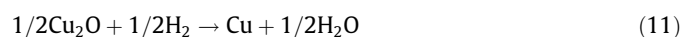


Fig. 13. AAC/UBC process conceptual flow diagram.



Chloride solutions offer the stability to monovalent copper (cuprous ions precipitate only at solution pH > 9, cupric ions readily precipitate at solution pH of 3–4) and sulfur reports to the leaching residue in its elemental form compared with sulfuric acid leaching, where copper and sulfur are oxidized to higher oxidation stages of 2+ and 6+, respectively (Hyvärinen et al., 2004). Nevertheless, one challenge in chloride media is the need for special construction materials due to their corrosive nature. The HydroCopper® chloride process has reached commercial maturity scale in Mongolia and at the Morenci mine in Arizona (Turkmen and Kaya, 2009). However, the process has not been used to date in conjunction with PGMs and copper–gold ores.

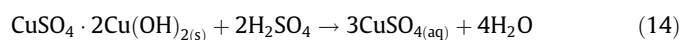
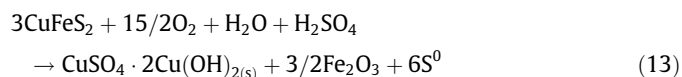
3.2.4. Sulfate-based leach processes

3.2.4.1. Processes using partial pressure oxidation.

3.2.4.1.1. Cominco Engineering Services Ltd. process (CESL process).

The CESL process, schematized in Fig. 12, is a hydrometallurgical alternative to copper sulfide concentrates smelting. The process was later expanded to include process development on other base metals as well as precious metals recovery. The process is composed of two leaching stages. The first is a pressure oxidation (150 °C, 700 kPa O₂, 1100 kPa total pressure) with chloride (12 g/L Cl⁻) as a catalyst to produce CuSO₄·Cu(OH)₂ which is leached by sulfuric acid and, then the leaching residue is fed to the second atmospheric leach (Eqs. (13) and (14)). Gold is recovered from the residue by cyanidation following elemental sulfur removal (using organic solvent: hot perchloroethylene), so that cyanide consumption is reduced (Carneiro and Leão, 2007). The

process converts iron to hematite, and sulfur to elemental sulfur (Wang, 2005).



Precious metals recovery from the residue would be complicated by the elemental sulfur presence, which would tend to pick them up from the pregnant rich leach solution rendering the approach unattractive (Milbourne et al., 2003). Note that this applies to a number of processes mentioned earlier as well. According to Dreisinger (2006), the CESL technology has completed a feasibility study for its application in copper process in Brazil.

3.2.4.1.2. The Anglo American Corporation/UBC process (AAC/UBC). The Anglo American Corporation/University of British Columbia (AAC/UBC) copper process, presented in Fig. 13, is a medium temperature leach process for chalcopyrite concentrates. The concentrates are reground to fine size (P₈₀ of 5–20 µm) and leached under moderate pressure (700 kPa O₂) at 150 °C in an acid–sulfate system (Dreisinger, 2006). Leaching of CuFeS₂ at 150 °C in the presence of elemental sulfur requires process conditions that prevent coating of unreacted CuFeS₂ by liquid sulfur and avoidance of passivation (melting point of sulfur is 125 °C). The passivation is not necessarily totally removed. The problem is addressed by either: (1) elemental sulfur removal before PGM leaching or (2) interaction of PGM leaching reagents with elemental sulfur.

Surfactant additives such as calcium lignosulfonate and orthophenylenediamine can be used to disperse the molten sulfur. However, depending on the amount of oxygen provided, sulfide sulfur in CuFeS₂ may be oxidized to either elemental sulfur or to sulfate according to the reactions in Eqs. (15) and (16). High

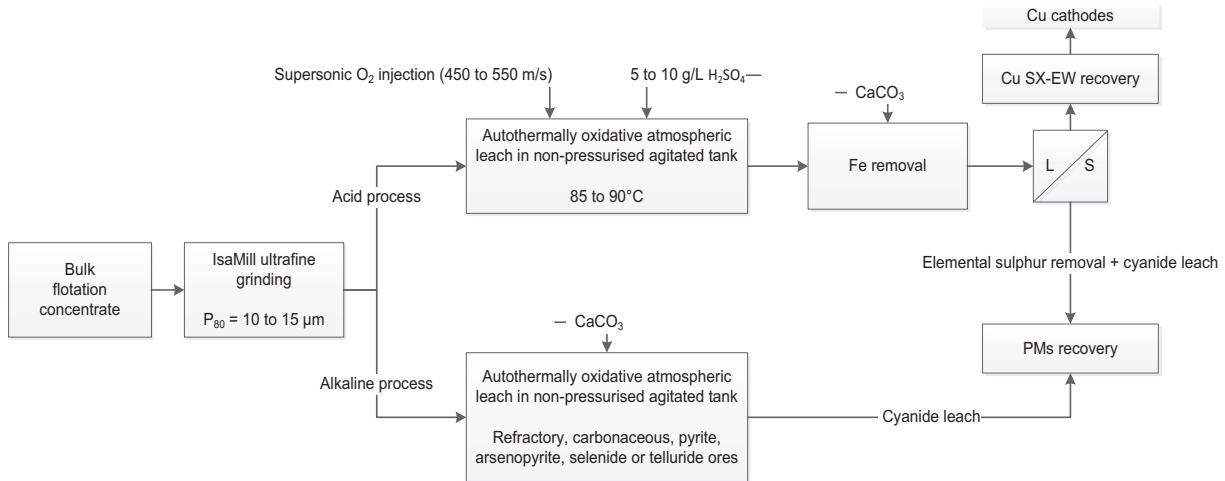
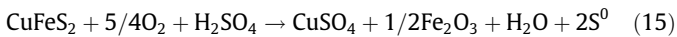


Fig. 14. Albion process conceptual flow schematic for base and precious metals recovery.

elemental sulfur yields (Eq. (15)) may be desirable to reduce oxygen consumption. A further major advantage is that a possible saleable by-product is produced instead of the sulfate, which requires lime for neutralization. In addition, the cost of oxidizing the concentrate is only about 30% of that for the higher-oxygen demand where sulfate is produced (Eq. (16)). Copper is recovered by conventional SX-EW, while precious metals can be recovered by leach residue cyanidation following elemental sulfur removal. The AAC/UBC copper process has not yet been applied commercially. The process has been evaluated in a continuous, fully integrated pilot plant simulation test program (Dreisinger, 2006).

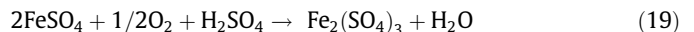
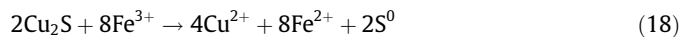
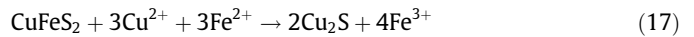


3.2.4.1.3. *The Albion process.* The Albion technology, schematized in Fig. 14, was developed by Xstrata Plc to treat concentrates produced from refractory base and precious metal ores. The technology is a sulfate based process employing ultrafine grinding (P_{80} of 10–15 μm) at temperatures of around 85–90 $^\circ\text{C}$, atmospheric pressure to accelerate the kinetics and increase copper recovery level from chalcopyrite, in conventional agitated tanks with corrosion resistant alloy steel shells (Nazari et al., 2012a; Kowalczyk and Chmielewski, 2008; Ellis et al., 2008). The Albion process is an auto-thermal operation, i.e. the leach slurry temperature is set by the amount of heat released in the leaching reaction.

Both the Albion and ActivOx[®] processes make use of ultrafine grinding to achieve sulfide dissolution (enhanced matrix attack) at lower temperature and pressures than required by conventional high pressure oxidation (Ellis et al., 2008). Note that fine grinding produces particles with P_{100} of <38 μm while ultrafine grinding

produces particles sized within 1 and 20 μm range (La Brooy et al., 1994). Ultrafine grinding performs the same function as roasting, pressure oxidation, bio- and chemical oxidation which is to break down the sulfide matrix to liberate precious metals locked in silicates or other minerals (Flatman et al., 2010).

According to Hourn et al. (2005), ultrafine grinding of sulfide minerals to particle size of 80% passing 8–12 μm will eliminate mineral passivation by sulfur precipitates, as the leached mineral will disintegrate prior to the precipitate layer becoming thick enough to passivate it. The oxygen used for oxidation is injected into the base of the Albion leach reactor at supersonic velocity to achieve the required mass transfer and leaching rate. Chalcopyrite is acid leached through ferrous ion oxidation (Fe^{3+} being the main oxidizing agent) by oxygen according to the mechanism suggested by Hiroyoshi et al. (2001) in Eqs. (17) and (18). Ferrous oxidation by oxygen takes place as in Eq. (19).



Copper is extracted via SX-EW to produce copper cathodes (Kowalczyk and Chmielewski, 2008). Excess sulfide sulfur in chalcopyrite leaching is present in the residue as elemental sulfur. This makes precious metals recovery difficult as S^0 can form a protective coating on the mineral particles. Once present, the coating may hinder the leaching process or even stop it completely. Jeffrey and Anderson (2003) and Lu et al. (2000) have suggested non-cyanide leaching methods such as sodium hydroxide to overcome elemental sulfur issues.

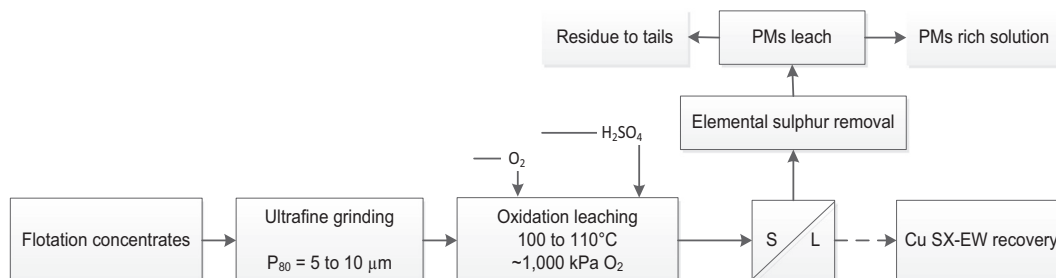
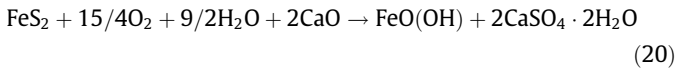


Fig. 15. ActivOx[®] process conceptual flow schematic.

Oraby and Eksteen (2013) have shown that one can leach copper sulfides (including chalcopyrite), oxides and native copper effectively from a copper mineral-precious metal concentrate using an alkaline glycine solution at pH of 10–11 with hydrogen peroxide as oxidant. The copper glycinate solution can be treated for copper recovery by a number of conventional technologies such as precipitation using NaSH or solvent extraction. Elemental sulfur formation is prevented by performing the oxidation in alkaline glycine solution.

Hourn et al. (2005) have reported that Albion leach process can operate under either acidic or alkaline conditions (see Fig. 14). In the first case (acid leach), base metals are extracted along with precious metals as by-product, while in the second case; precious metals encapsulated in pyrite, arsenopyrite, selenide or telluride ores are alkaline leached with no requirement of recovering base metals. The alkaline leach process of refractory precious metal bearing sulfides such as pyrite progresses through pyrite dissolution (Eq. (20)) to finally expose the precious metals for subsequent cyanidation.



The Albion process is commercially operational at two plants treating zinc sulfide concentrates that are located in Spain and Germany, while a third Albion process plant operating in the Dominican Republic is treating refractory gold/silver concentrates (Turner and Hourn, 2013).

3.2.4.1.4. *The ActivOx[®] process.* The ActivOx[®] process (sulfate based process), shown in Fig. 15, is a low pressure oxidation technology developed to recover a range of base and precious metals from sulfide ores and concentrates (Palmer and Johnson, 2005). The process incorporates ultrafine grinding – typically P₈₀ of 5–10 μm to activate mineral surfaces – followed by a low-pressure leach of around 1000 kPa O₂ at low-temperature of 100–110 °C to break down the sulfide matrix within a retention time of 1–2 h (Gok and Anderson, 2013; Palmer and Johnson, 2005; La Brooy et al., 1994). Matrix disintegration by high energy grinding is also called “mechanical activation” (Balaz et al., 2000; Maurice and Hawk, 1999).

The total surface area increases by decreasing the initial mineral particle size, which leads to increasing internal and surface energies, decreasing the coherence energy of solids and finally increasing copper extraction. The leaching temperature in this process is lower than the sulfur melting point of 125 °C, hence surfactant addition is not required. The oxidation reactions in the ActivOx[®] process occur through reactions in Eqs. (21)–(23).

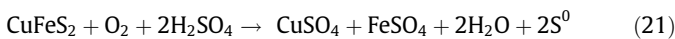
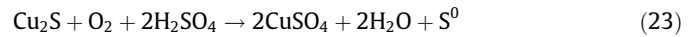
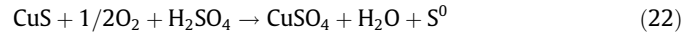


Table 1
Relative potentials of some hydrometallurgical oxidizers (Anderson, 2003).

Oxidant	Redox equation	E _R ⁰ in mV (pH = 0, H ₂ reference)
Fe ³⁺	Fe ³⁺ + e ⁻ → Fe ²⁺	770
HNO ₃	NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO _(g) + 2H ₂ O	957
HNO ₂	NO ₂ ⁻ + 2H ⁺ + e ⁻ → NO _(g) + H ₂ O	1202
O _{2(g)}	O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	1230
Cl _{2(g)}	Cl _{2(g)} + 2e ⁻ → 2Cl ⁻	1358
NO ⁺	NO ⁺ + e ⁻ → NO _(g)	1450



Elemental sulfur formed in the process remains in the leaching residue, which leads to difficulties in precious metals recovery. Base metals are recovered from the solution via solvent extraction, while precious metals in the leach residue are recovered by conventional cyanidation treatment following elemental sulfur removal. Most of iron precipitates as goethite or hematite. Problems have been noted in the prevention of magnesium and calcium accumulation which would affect nickel solvent extraction using versatic acid and copper electrowinning. Several researchers (Lorenzen et al., 2009; Eksteen et al., 2008; Georgalli et al., 2008) have looked at partial calcium and magnesium removal using ammonium fluoride to precipitated fluorite (CaF₂) and sellaite (MgF₂) with alumina based adsorption to remove excess fluoride ions. The ActivOx[®] process for copper was demonstrated at the Tati Hydrometallurgical Demonstration Plant (THDP) in 2004 (Palmer and Johnson, 2005).

3.2.4.1.5. *The Nitrogen Species Catalyzed (NSC) process.* Gok (2010) stated that the basic principle underlying leaching with oxy-nitrogen species is the recovery of valuable metals occluded within sulfide mineral grains in sub-microscopic form as inclusions or in solid solutions, by oxidizing sulfide either to elemental sulfur or sulfate with an oxidant and thereby destroying the sulfide lattice. The NSC process is a sulfate leach system augmented with 2 g/L NaNO₂ and operating under mild conditions such as 125 °C, 400 kPa O₂ (Milbourne et al., 2003). The process does not require excessively high temperatures or pressures, and has no corrosion issues to deal with; hence commonly available stainless steel can be used for the reactor vessel (Anderson, 2003). Fig. 16 illustrates the simplified Nitrogen Species Catalyzed (NSC) process flowsheet.

The complex chalcopyrite leaching chemistry in acidic nitrite electrolyte is shown in Eqs. (24) and (25) (Gok and Anderson, 2013).

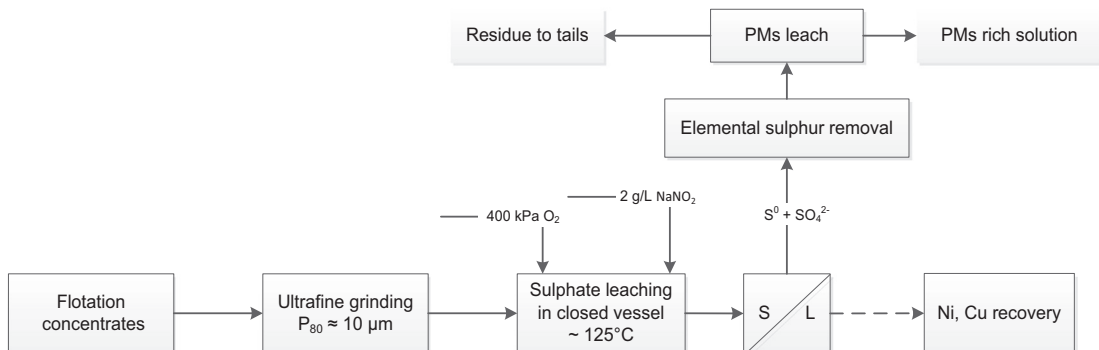


Fig. 16. Nitrogen Species Catalyzed (NSC) process conceptual flow schematic.

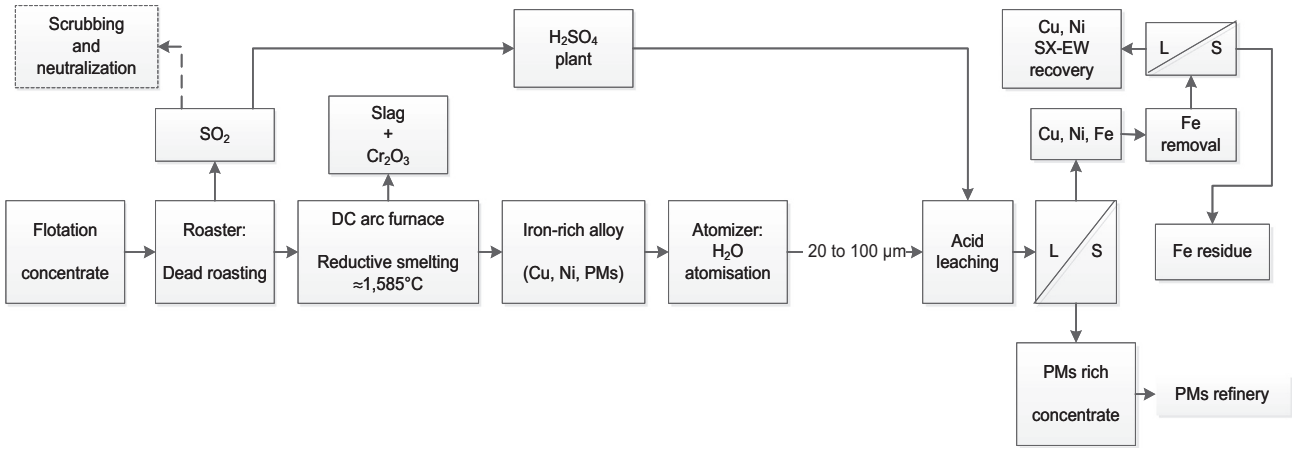
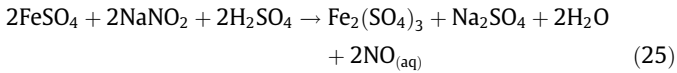
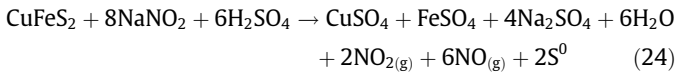
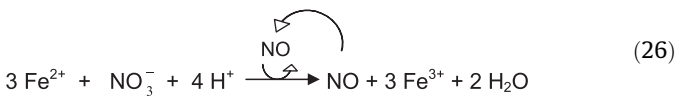


Fig. 17. ConRoast process conceptual flow schematic.



From Table 1 it can be seen that NO⁺/NO couple is capable of an extremely high redox potential compared to other well-known redox couples.

During the leach process, in addition to NO_(g) and NO_{2(g)}, the system may contain a number of other nitrogen compounds (HNO₂, N₂O₄, NO₂⁻, N₂O₃, HNO₃, NO₃⁻, etc.) that have various catalytic activities. Nitrous acid (HNO₂) has been predicted to be the most kinetically reactive form (Gok et al., 2013). Previous work done by Epstein et al. (1980) has indicated that the reaction between nitric acid and nitric oxide products proceeds auto-catalytically (Eq. (26)). Nitrogen species (oxidant) are continuously regenerated in a closed vessel with an oxygen overpressure (Anderson, 2003).



In the NSC process, precious metals can either be leached or retained in the oxidized solids by controlling the chosen process conditions (Milbourne et al., 2003). According to Anderson (2003), gold leached by the alkaline sulfide system (this is used owing to the elemental sulfur present in the residue solids) is readily

recoverable by electrowinning, gaseous precipitation, chemical precipitation, cementation, solvent extraction, or ion exchange. The Nitrogen Species Catalyzed pressure leaching process (NSC) was commissioned and performed successfully on an industrial scale at Sunshine Precious Metals (Gok and Anderson, 2013).

3.2.4.1.6. *The ConRoast process.* Mintek (Jones, 2002) has developed and piloted a patented process for the treatment of nickel–copper–PGM sulfide concentrates with high chromite and low sulfur content. The ConRoast process is based on sulfur removal by fluidized-bed roasting, followed by a reductive smelting of the dead-roasted (with low sulfur content) concentrate in a DC arc furnace. The process uses an iron-based alloy as a collector of nickel, copper, cobalt and PGMs rather than matte-based procedure; because there is effectively no sulfur present at this stage of the process (smelting). The smelted alloy is then atomized to produce fine particles sized between 20 and 100 μm, subjected to hydrometallurgical acid leaching to remove the iron, extract the base metals and leave a PGM rich final concentrate suitable as direct feed to PGM refineries (Jones, 2009; Braemore resources Plc., 2009; Phillips et al., 2008). The conceptual flow schematic of the process is depicted in Fig. 17.

In order to avoid the commonly experienced problem of magnetite or chromite spinel build-up in the furnace, this latter is operated under quite strongly reducing conditions at high temperatures averaging 1585 °C (Geldenhuys and Jones, 2009). This constitutes its main disadvantage; as roasting, smelting, SO₂ gas scrubbing and neutralisation are required similar to conventional smelting processes. Sulfur emissions are captured and

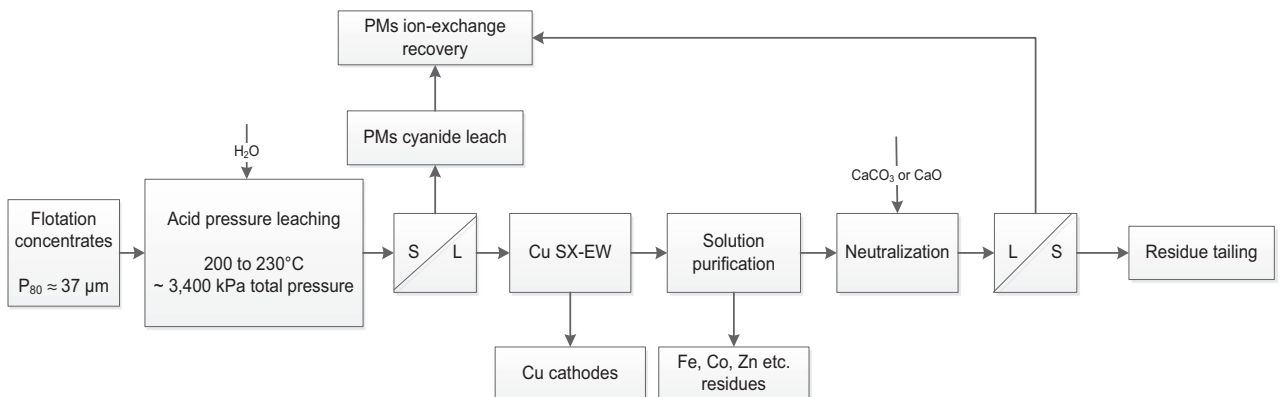
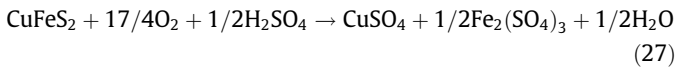


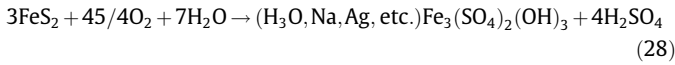
Fig. 18. Conceptual flow schematic of the Total Pressure Oxidation process.

removed from the enclosed roasting equipment in a continuous stream of sulfur dioxide gas, which is fed to a secondary plant to produce sulfuric acid for use in downstream base metal leaching operations (Phillips et al., 2008). In the case of low-sulfur feed materials, the gas is scrubbed and neutralized. Since October 2007, Braemore has successfully treated low-PGM content, high-chrome smelter feed at its ConRoast demonstration facilities using Mintek’s DC arc furnace in Johannesburg, South Africa (Braemore resources Plc., 2009).

3.2.4.2. Total Pressure Oxidation process (TPOX). The Total Pressure Oxidation process has been developed by Placer Dome and the University of British Columbia (UBC). The process has no suitable chelating agent. It uses water as leach medium and converts most of the sulfide sulfur to copper sulfate and sulfuric acid (Milbourne et al., 2003). The autoclave operates at typical conditions of 210–220 °C, with sparged oxygen to maintain 700 kPa overpressure (Wang, 2005). Chalcopyrite oxidation occurs through the reaction in Eq. (27), and the conceptual flow schematic of the process is shown in Fig. 18.



The Total Pressure Oxidation process has the advantage of rapid, complete copper recovery with high degree of iron hydrolysis and impurity fixation. Iron is rejected as a stable hematite phase (Fe₂O₃), which is one of the preferred hydrometallurgical process residues (Dreisinger, 2006). Hydronium jarosite is precipitated as a co-product which will collect silver (if present) and other monovalent cations via the reaction shown in Eq. (28) (Wang, 2005).



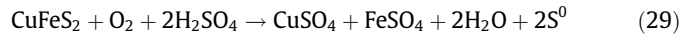
Precious metals follow iron and report to the hematite residue as an oxide or in elemental form. A secondary leach (cyanidation) is required to recover precious metals. The process is ideally suited to copper–precious metal concentrates. This because all sulfides are oxidized to sulfate and no cyanide-consuming sulfur reports to the residue, which would allow easy and economic precious metals recovery. However, the process oxidizes all sulfide minerals to sulfates and sulfuric acid (high oxygen consumption). Hence the

cost associated with high maintenance and sulfate disposal may become prohibitive, unless the copper/precious metals grade is high enough to warrant such neutralisation expense (Nazari et al., 2012a).

The sulfuric acid must be used beneficially for the process to be commercially viable since the cost of generating and neutralizing this acid is prohibitively high (Dreisinger, 2006; Marsden et al., 2003). For instance the acid can be used for heap leaching (Nazari et al., 2012c). The Total Pressure Oxidation technology has been implemented by Phelps Dodge at Bagdad, Arizona (Dreisinger, 2006). It has also been successfully commercialized at First Quantum’s Kansanshi Copper Operation in Zambia (Nazari, 2012).

3.2.5. Galvanically-assisted chalcopyrite leach process: Galvanox™

The Galvanox™ process (galvanically-assisted atmospheric leaching in a ferric/ferrous sulfate medium) developed by Dixon and Tshilombo (2005) for copper leaching from chalcopyrite, uses galvanic contact between chalcopyrite (as both anode and cathode) and pyrite (as cathode for ferric reduction) under controlled conditions (silver-activated pyrite as catalyst) to leach chalcopyrite concentrates at 80 °C (Nazari et al., 2012b,c). The overall leaching reaction is in Eq. (29) (Nazari et al., 2011, 2012a; Córdoba et al., 2008; Kowalczyk and Chmielewski, 2008).



Although ferric ion oxidizes the mineral sulfide, it may also be responsible for its passivation, because high [Fe³⁺]/[Fe²⁺] ratios of >>1 favor Fe³⁺ precipitation and nucleation as jarosite on the chalcopyrite surface and its later passivation (Córdoba et al., 2008). Silver is preferentially incorporated into the jarosite structure to form argentojarosite, AgFe₃(SO₄)₂(OH)₆ and loses its activity as catalyst. This is one of the main drawbacks associated with the technology (Nazari et al., 2012a). In addition, silver is expensive and would typically be avoided in practice as catalyst, unless the ores themselves contained sufficient silver. Finally, according to Nazari (2012), in this process PGM recovery is feasible through cyanide or thiosulfate leaching of copper residues. The Galvanox™ process has been evaluated in a continuous pilot plant simulation test program (Dreisinger, 2012; Nazari et al., 2012c). The conceptual flow schematic of the process is shown in Fig. 19.

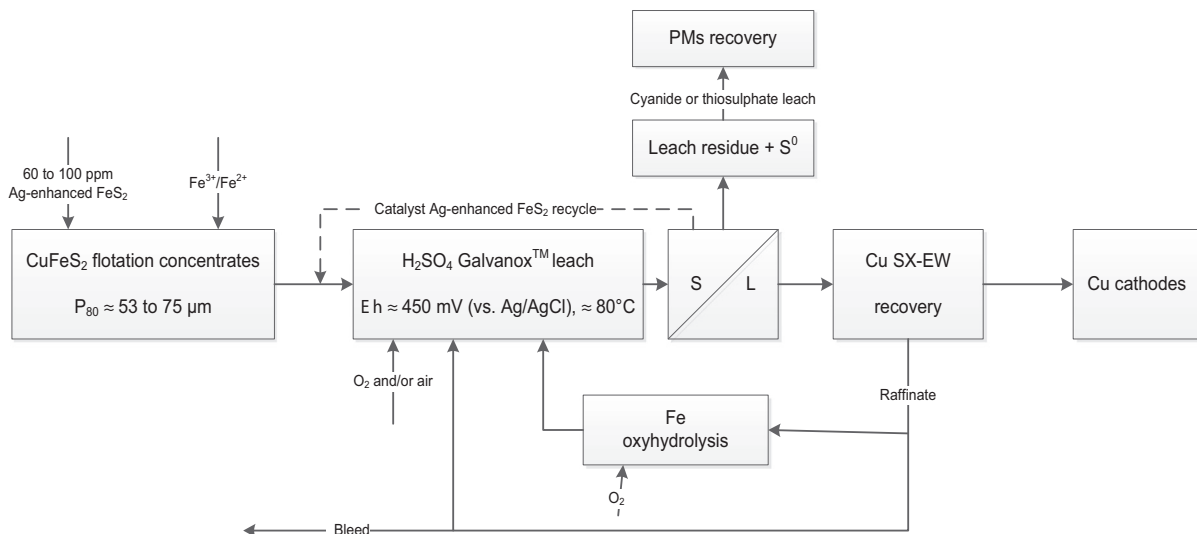


Fig. 19. Conceptual flow diagram of galvanically-assisted chalcopyrite leach process.

Table 2
Summary of operating features of some selected processes for exposing and/or extracting precious metals from copper sulfide materials.

Lixiviant	Process	P ₈₀ grind size (μm)	Leaching temperature (°C)	Pressure (kPa)	Special conditions	Sulfur product	Leaching time (h)	Status	References
Sulfate	AAC/UBC	5–20	150	700	Uses surfactants	S ⁰ /SO ₄ ²⁻	1	P	4, 14
	ActivOx [®]	5–10	100–110	1000	Uses ultrafine grinding	S ⁰ / SO ₄ ²⁻	1–2	D	1, 2, 3, 14
	Albion	10–15	85–90	Atm.	O ₂ injected at 450–550 m/s	S ⁰	22	C	1, 19, 20, 21, 24
	Galvanox [™]	53–75	80	Atm.	60–100 ppm Ag as catalyst	S ⁰	<12	P	22, 23, 24
	Total Pressure Oxidation	37	200–230	3400	H ₂ O as leach medium	SO ₄ ²⁻	1	C	4, 5, 6, 14
	ConRoast	–	–	–	Atm.	H ₂ O atomisation: 20–100 μm	–	–	D
Chloride	Intec Copper	–	85	Atm.	Mix of NaCl/NaBr + Cu ²⁺	S ⁰	16	D	2, 6, 10, 18, 24
	HydroCopper [®]	–	80–100	Atm.	pH = 1.5–2	S ⁰	10–20	C	15, 16, 17
Sulfate + Chloride	CESL	40	150	1100	10–15 g/L Cl ⁻	S ⁰	1–2	F	4, 6, 14
	Platsol [®]	15	≤220	3200	5–20 g/L Cl ⁻	SO ₄ ²⁻	1.2	F	4, 6, 11, 12, 14
	Kell	–	200–225	3000	Roasting residue at 900 °C	–	–	P	11
Sulfate + Nitrogen	NSC	10	125	400	H ₂ SO ₄ medium + 2 g/L NaNO ₂ in closed vessel	S ⁰ / SO ₄ ²⁻	0.5	C	6, 14, 14
Cyanide	Panton	38	60	Atm.	pH = 9.2; 5% Cr	SO ₂	100	B	13

Status: B – basic principles observed and reported, P – pilot plant, D – demo plant, F – final feasibility study, C – commercial scale maturity/Dashes indicate datum not available.

References: 1 – Nazari et al. (2012a,b,c); 2 – Palmer and Johnson (2005); 3 – La Brooy et al. (1994); 4 – Dreisinger (2006); 5 – Wang (2005); 6 – Milbourne et al. (2003); 7 – Jones (2009); 8 – Braemore resources Plc. (2009); 9 – Phillips et al. (2008); 10 – Sammut and Welham (2002); 11 – Liddell and Adams (2012); 12 – Cole and Joe Ferron (2002); 13 – Lewins and Greenaway (2004); 14 – Gok and Anderson (2013); 15 – Lundström et al. (2005, 2009); 16 – Senanayake (2009); 17 – Turkmen and Kaya (2009); 18 – Moyes and Crescent (1999); 19 – Kowalczyk and Chmielewski (2008); 20 – Ellis et al. (2008); 21 – Turner and Hourm (2013); 22 – Dixon and Tshilombo (2005); 23 – Dreisinger (2012); 24 – Nazari (2012).

3.3. Summary

Although by no means exhaustive, Table 2 presents a cursory summary of existing technologies in the extractive metallurgy of low-grade refractory precious metal sulfide ores and concentrates.

4. Use of unconventional lixivants

Considerable research efforts have been made in investigating alternatives to cyanidation for gold. The non-cyanide systems that have been considered include halogens, thiourea, thiosulfate, thiocyanate and the newly developed alkaline glycine leach (Oraby and Eksteen, 2014; Zhang et al., 2012; Li and Miller, 2006; Aylmore, 2005). Gold forms a large number of complexes with these ligands such as AuCl₄⁻, Au[SC(NH₂)₂]₂⁺, Au(S₂O₃)₃³⁻, Au(SCN)₂⁻, and Au(NH₂CH₂COO)₂⁻. However, some of these alternative lixivants have not been industrially tested on PGMs. It is the aim of this part of the investigation to provide a status evaluation of PGM leaching using the aforementioned lixivants.

4.1. Alkaline glycine leach processes

The Western Australian School of Mines (WASM) at Curtin University in Perth, Western Australia has developed and patented

Table 3
Stability constants for a selection of gold, platinum and palladium compound complexes at 25 °C.

Ligand (n)	log β _n (Au ⁺ /Au ³⁺)					log β _n (Pt ²⁺)					log β _n (Pd ²⁺)				
	1	2	3	4	References	1	2	3	4	References	1	2	3	4	References
I ⁻	–	19.2	–	47.7	2	–	24.4	27.9	29.6	1	10.0	–	–	24.9	1
Cl ⁻	–	9.71	–	25.3	2	4.97	8.97	11.89	13.99	1	4.47	7.76	10.17	11.54	1
Br ⁻	–	12.7	–	32.8	2	4.9	9.0	12.6	15.4	1	5.17	9.42	12.7	14.9	1
SC(NH ₂) ₂	–	23.3	–	–	2	–	–	–	–	–	–	–	–	–	–
S ₂ O ₃ ²⁻	–	26.24	–	–	2	–	–	–	43.7	1	–	–	–	35.0	1
SCN ⁻	–	17.2	–	43.9	2	–	–	–	33.6	1	–	16.19	–	25.6	1
CN ⁻	–	38.3	–	85	2, 3, 4, 6	–	–	–	41.0	5, 6	–	–	–	63	1

References: 1 – Mountain and Wood (1988); 2 – Senanayake (2004b); 3 – Deschenes (2005); 4 – Aylmore (2005); 5 – Muir and Ariti (1991); 6 – Mpinga et al. (2014). Dashes indicate datum not available.

a hydrometallurgical method suitable to treat low-grade copper-gold sulfide deposits (Oraby and Eksteen, 2014). The amino-acid lixiviant containing glycine and peroxide showed copper dissolution of 98% within 48 h, at ambient conditions and solution pH of 10.5–11. The results also showed that 100% of chalcocite (Cu₂S), cuprite (Cu₂O), metallic copper and about 80% of chalcopyrite (CuFeS₂) in the concentrate were dissolved (Oraby and Eksteen, 2014). Pyrite (FeS₂) remained intact during the leaching time.

The alkaline glycine leach process is still in its infancy. However, it does offer an attractive potential for treating low-grade refractory ores and flotation concentrates. It is an optimistic hope that alkaline glycine leach may find applications in the lower-grade PGM deposits treatment by using heaps, dumps or *in situ* leaching techniques similar to those practiced in the gold industry, since the leaching conditions are almost identical. Nevertheless, more work is needed to evaluate different metal recovery methods and the possibility of regenerating and recycling the lixiviant.

4.2. Halide system (bromide, chloride and iodide) leach processes

Halide leaching includes bromide, chloride and iodide. They are well known lixivants for gold, being used before the introduction of cyanide (Rosia, 2007). According to La Brooy et al. (1994), chlorination was practised in Australia as early as 1891. The halide

system offers high leaching rates (Zhang et al., 2012). However, halogens have proved to be very reactive with other ore minerals, especially sulfides. Hence under typical halide-leaching conditions, reagent consumptions would be very high if the ore contains significant sulfide minerals (Aylmore, 2005). Halide system was limited to analytical applications and PGM refineries, where the dissolution speed and capacity for simultaneous sulfide destruction are more important than reagent consumption.

4.2.1. Iodide leach processes of precious metals

Iodine forms the most stable gold complexes (see Table 3) of all the halogens (Zhang et al., 2012). Prasad et al. (1991) stated that iodine leaches gold from its ores at low concentrations and can penetrate rocks particularly well. Solid iodine reacts with iodide in aqueous solution to form triiodide ions (the major oxidant). This then reacts with gold to give Au(I) rather than forming Au(III) complex (Eqs. (30) and (31)). According to Aylmore (2005), Au(III) complex is not stable (E° for $\text{AuI}_2^- < \text{AuI}_4^-$), it oxidizes iodide ion to iodine and Au(III) complex is reduced to Au(I). La Brooy et al. (1994) found that gold leaching rates in iodide solutions are much faster than conventional cyanidation. Typical iodide gold leaching conditions are 1 g/L I_2 , 9 g/L NaI, solution pH of 4–9 and standard redox potential of about 336 mV (vs. SCE) (Sparrow and Woodcock, 1995).



Dawson and Kelsall (2007) have used Eh–pH diagrams to interpret platinum and palladium dissolution behavior in halide solutions including iodide, chloride and bromide. Selective PGM dissolution in less acidic and aggressive conditions could be achieved by the iodide system, as Pd(II/IV) and Pt(II/IV) stabilities regions covered a wide solution pH range. The major platinum/palladium-iodide complex ions under acidic conditions are PtI_6^{2-} and PdI_4^{2-} . The oxidation and reduction reactions are presented in Eqs. (32)–(33) and (34), respectively (Jha et al., 2013; Zanjani and Baghalha, 2009).



No single industrial operation using iodide/iodine for PGM leaching has been reported.

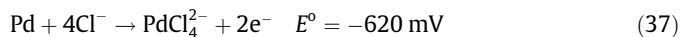
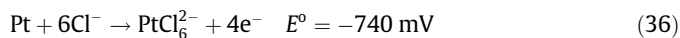
4.2.2. Chloride leach processes of precious metals

Chlorination was used extensively for pre-treating refractory and carbonaceous ores in several plants in the USA in the 1980s (Aylmore, 2005). The leaching reaction with chlorine (oxidizing agent) is very fast but, as with cyanide, the process is not selective since almost all metals form very stable chloro complexes (Farinha et al., 1992). According to Aylmore (2005), the complex AuCl_2^- is formed initially and is rapidly oxidized to AuCl_4^- . The general reaction is described in Eq. (35). It is worth mentioning Baghalha (2012) who observed that the gold-chloride complex was unstable and could re-precipitate upon contact with a reducing mineral, such as chalcocopyrite. Typical chloride gold leaching conditions are 5–10 g/L Cl_2 , 5–10 g/L NaCl, solution pH of <2 and standard redox potential of about 752 mV (vs. SCE) (Sparrow and Woodcock, 1995).



However, the most stable platinum and palladium chloro complexes are PtCl_6^{2-} and PdCl_4^{2-} , respectively (Mahmoud, 2003). In the Eh–pH diagrams (not shown), PtCl_6^{2-} predominates over a wide acidic area and high potential regions; PdCl_4^{2-} predominates in

acidic and lower potential regions (Harjanto et al., 2006; Mahmoud, 2003). The standard electrode potentials for platinum and palladium metal solubilization in aqueous chloride media are expressed by the half reactions in Eqs. (36) and (37). A standard potential higher than 740 mV is therefore required to oxidize a $\text{Pt}_{(\text{s})}$ and $\text{Pd}_{(\text{s})}$ mixture.



In general, PGM dissolution is based on providing high oxidation potential and effective complexing ions in solution (Mahmoud, 2003). Chlorination rates are favored by low pH, high chloride and chlorine levels, increased temperature and a large ore surface area (La Brooy et al., 1994). PGM chlorocomplex stability increases at higher chloride-ion concentrations in solution, and this increases their dissolution efficiency (Mahmoud, 2003).

Chlorine/chloride technology has been applied industrially on a significant scale (Zhang et al., 2012). The addition of a chloride salt to a moderate H_2SO_4 concentration stabilizes PGM ions in the solution by forming corresponding chloro complexes and hence improves their dissolution e.g. in the Platsol[®] process. However, chloride leaching requires special reactors such as glass-lined vessels to resist its highly corrosive conditions (Zhang et al., 2012; Lundström, 2009; Winand, 1991).

4.2.3. Bromide leach processes of precious metals

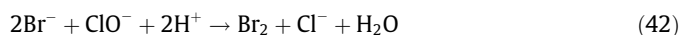
Bromine/bromide gold leaching from ores was reported as early as 1846 (Aylmore, 2005; Kuzugüdenli and Kantar, 1999). The natural advantages claimed for bromine are rapid extraction, non-toxicity and adaptability to a wide range of solution pH values (Prasad et al., 1991). Leaching in bromine solution shows much faster gold extraction kinetics with no worse copper dissolution compared to the alkali systems (Vukcevic, 1996; La Brooy et al., 1994). Meersbergen et al. (1993) recorded similar gold extraction levels for both cyanide and bromine/bromide solutions, while the leaching kinetics for the bromide system were about four times faster than those obtained with cyanide. Typical bromide gold leaching conditions are 2–5 g/L Br_2 , 0–10 g/L NaBr, solution pH of 5–6 and standard redox potential of about 612 mV (vs. SCE) (Sparrow and Woodcock, 1995).

As noted earlier, Dawson and Kelsall (2007) have discussed the use of Eh–pH diagrams to interpret platinum and palladium dissolution behavior in halide solutions including bromide. The predicted Pd and Pt behaviors in bromide media are similar to those in chloride media, although with slightly larger stability regions for the aqueous bromo complex species which extend to some extent to more alkaline pH's than in chloride media. So it may be possible to leach PGMs selectively in bromide, but the solution pH would need to be more acidic. Dadgar et al. (1997) have suggested that gold, platinum and palladium dissolution in bromine solutions proceeds according to Eqs. (38)–(40).



For platinum dissolution from Pt compounds such as platinum oxide, a redox potential of about 850–1250 mV is required. The redox potential required to dissolve Pd is about 500–750 mV (Dadgar et al., 1997). Due to the high potential required to produce precious metal-bromide complexes from the metal, the addition of a strong oxidant such as bromine is needed. Bromide can also be added to the leaching solution along with chlorine (e.g. in the

Intec process) or hypochlorite (as oxidant), to generate bromine *in situ* as shown in Eqs. (41) and (42) (Kuzugüdenli and Kantar, 1999).



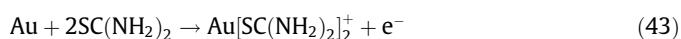
Zhang et al. (2012) stated that special equipment is required for managing the safety and health risks in bromide leaching processes, due to the volatility of bromine which has a vapor pressure of 10 and 28 kPa at 0 and 35 °C, respectively. This restricts it from industrial applications. However, according to Aylmore (2005), the use of commercially available organic bromides (e.g., N-halo hydantoins such as Geobrome 3400) reduces problems with vapor losses. Another disadvantage of bromine use is likely to be high reagent consumption in the presence of reactive ore components such as sulfides (Prasad et al., 1991). Finally Wan et al. (1993) found that neutral poly-acrylic ester adsorbents such as XRD-7 and XRD-8 (which are resistant to hypochlorite oxidation) can be used for precious metals recovery from halide solutions. It is believed that there are no commercial scale operations using this technology for PGM leaching.

4.3. Thiosystem (thiosulfate, thiocyanate and thiourea) leach processes

The thiosystem leaching includes thiourea, thiosulfate and thiocyanate. The lack of information in literature on the ability to regenerate and recycle leaching solutions (minimizing lixiviant consumption) increases the importance of research in this field. However, the thiosystem forms stable complexes with precious metals (Table 3), intermediate to the chloride and cyanide complexes both of which have been shown sufficiently stable for industrial use.

4.3.1. Thiourea leach processes of precious metals

Gold dissolves in acidic thiourea solutions forming cationic complexes (anodic half reaction in Eq. (43)). One of the important features of thiourea [SC(NH₂)₂, or Tu] gold dissolution is that the leaching can be performed in acidic media, enabling the use of soluble oxidizing agents such as ferric salts (Eq. (44)) (Li and Miller, 2006; Munoz and Miller, 1999). The leach reaction is rapid and according to Prasad et al. (1991), gold extractions of up to 99% can be achieved in acidic conditions (solution pH of about 1.4) within 10–15 min. Typical thiourea gold leaching conditions are 0.1–1% Tu, 0.2% Fe³⁺ and solution pH of 1–2 (Sparrow and Woodcock, 1995).



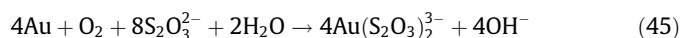
It is pertinent to note that the standard redox potential for the reaction in Eq. (44) equals 420 mV and that of Fe³⁺/Fe²⁺ is 770 mV. Hence ferric ion may oxidize thiourea during gold leaching if it is used as oxidant (Li and Miller, 2006). La Brooy et al. (1994) have argued that Eh values of 400–600 mV are required for significant gold dissolution rates with ferric ion in the leach system. Wan et al. (1993) have concluded that it was necessary to maintain the leaching potential between 420 to 450 mV (vs. SHE) in order to limit thiourea decomposition and to optimize gold extraction.

Thiourea has long been known to form extractable complexes (its involvement in elution/stripping processes) with both platinum and palladium (Schoeman et al., 2012; Dunne et al., 2009; Tatarnikov et al., 2004; Green et al., 2004). However, it would seem that no work has been conducted on leaching PGM ores/concentrates using thiourea as no literature could be found.

Finally despite its low acute toxicity, thiourea is not a safe reagent at all. It is a potent thyroid poison for humans, and recognized as potentially carcinogenic where chronic exposure is possible (Rosia, 2007; Kuzugüdenli and Kantar, 1999). Nonetheless, Li and Miller (2006) have an opposed view in this matter, they have argued that thiourea has been shown to be a carcinogen for rats and possibly for trout. They also pointed out that thiourea has been used for years in thyroid disease treatment for humans and thereby considered to be non-carcinogenic to humans.

4.3.2. Thiosulfate leach processes of precious metals

The use of thiosulfate (S₂O₃²⁻) for gold extraction has been reported as early as 1880 (Prasad et al., 1991). Sodium thiosulfate and ammonium thiosulfate are the two salts commonly used in gold leaching (Zhang et al., 2012). Thiosulfate is stable in alkaline medium. Hence alkaline solutions are used to prevent its decomposition by acid although gold thiosulfate complex is quite stable once it has formed (La Brooy et al., 1994). Two patents were assigned to Kerley (1983) for sulfite ions addition in order to stabilize thiosulfate solutions during gold leaching reactions. Sulfite ions react with any sulfide ions in solution, thereby preventing metal sulfides precipitation. The overall stoichiometry for gold dissolution in alkaline aqueous thiosulfate solutions, and in the presence of oxygen is expressed in Eq. (45) (La Brooy et al., 1994).



Ammoniacal thiosulfate solution is suitable for leaching gold ores/concentrates containing alkaline components in the presence of copper, manganese and/or arsenic which are sensitive to cyanide leaching (Zhang et al., 2012). In contrast to thiourea and thiocyanate, gold dissolves slowly in alkaline thiosulfate, but the dissolution rate is markedly enhanced by the presence of ammonia and copper ions.

Grosse et al. (2003) observed that the activation energy required to dissolve metallic gold in the presence of ammonia at solution pH of 10, with excess thiosulfate and Cu(II), was 15.54 kJ/mol while in the absence of ammonia and Cu(II); the activation energy rises to 27.99 kJ/mol demonstrating the catalytic effects of ammonia and Cu(II). La Brooy et al. (1994) found that copper ions (catalytic oxidant) accelerated the gold dissolution rate twenty-fold. Typical thiosulfate gold leaching conditions are 0.2 M Na₂S₂O₃, 2 M NH₄OH, 3 g/L Cu, solution pH of ≥7, temperature of 50 °C and standard redox potential of about –89 mV (vs. SCE) (Sparrow and Woodcock, 1995).

Experimental investigations by Anthony and Williams quoted by Azaroual et al. (2001) showed that dissolved Pt concentrations rise sharply with S₂O₃²⁻ concentration. These researchers have indicated Pt(S₂O₃)₄⁶⁻ formation of which the stability was sufficiently high to guarantee platinum mobility. Pd(S₂O₃)₄⁶⁻ and Pt(S₂O₃)₄⁶⁻ complexes have aqueous solubilities above 10 ppb at solution pH of 7 and temperature of 25 °C. However, observations by Grosse et al. (2003) that the formed complexes are not thermodynamically stable, and slowly decompose into insoluble S-bridged oligomers, conflicts with conclusions reached by Mountain and Wood (1988) and Hancock et al. (1977) who have indicated stable Pt and Pd thiosulfate complexes do exist (see Table 3 and Fig. 20). Nevertheless, no single industrial operation using thiosulfate for PGM leaching has been reported.

4.3.3. Thiocyanate leach processes of precious metals

4.3.3.1. Gold thiocyanate acid leaching. Thiocyanate has been known for a long time to act as gold lixiviant (Adams, 2005; Broadhurst and du Preez, 1993). One of the thiocyanate system's important features is to leach precious metals in acidic solutions, thus avoiding problems related to neutralisation and material handling,

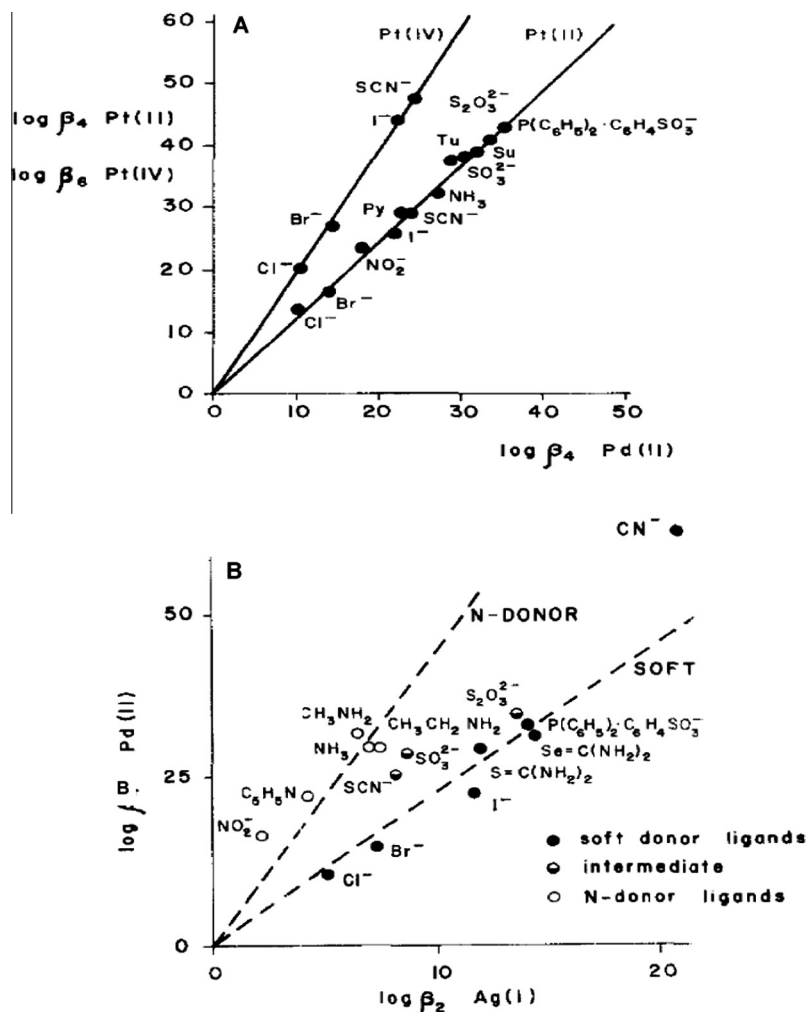
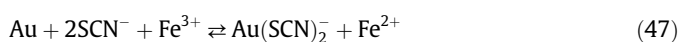
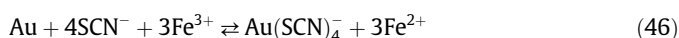


Fig. 20. (A) Linear free-energy relation for $\log(\beta_4, \beta_6)$ of Pt(II, IV) complexes plotted against $\log \beta_4$ for Pd complexes, (B) $\log \beta_4$ for Pd(II) complexes formation plotted against $\log \beta_4$ for Ag(I) complexes formation with the same ligand (Hancock et al., 1977).

especially for slurries after sulfide minerals pre-oxidation (Wan and LeVier, 2011; Li et al., 2008). Gold can be leached by 0.01–0.05 M SCN^- at potentials of around 400–450 mV and solution pH of 1–3 in the presence of either ferric ions 2–5 g/L or peroxide as oxidant (Aylmore, 2005). Generally, ferric available from sulfide mineral oxidation can be employed as oxidant for precious metals leaching. The standard oxidation potential for ferric to ferrous couple is 770 mV (vs. SHE).

However, the published lower and upper potential ranges for the formation of tetrathiocyano-auric [or aurithiocyanate: $\text{Au}(\text{SCN})_4^-$] and di-thiocyano-aurous [or aurothiocyanate: $\text{Au}(\text{SCN})_2^-$] show considerable discrepancy in the literature. For some authors, $\text{Au}(\text{SCN})_2^-$ forms at the upper potential range limit of about 691 mV (Li et al., 2012a,b,c; Senanayake, 2004b; Kuzugüdenli and Kantar, 1999; Broadhurst and du Preez, 1993), while for others it forms at the lower potential limit of around 659 mV probably as a result of thiocyanate oxidation by ferric ions (Li et al., 2008; Adams, 2005; Sparrow and Woodcock, 1995). The commonly reported and simplified reactions are written as in Eqs. (46) and (47).



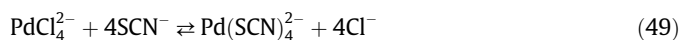
4.3.3.2. PGMs thiocyanate acid leaching. Platinum and palladium are known to form complexes with thiocyanate ion in solution (Kriek, 2008; Oleschuk and Chow, 1998; Al-bazi and Chow, 1984). Hamacek and Havel (1999) have found that Pt and Pd thiocyanate complexes present higher stability as compared with chloro complexes. Table 3 shows the stability constants of selected precious metal complex species that have been reported in literature. As can be seen, thiocyanate forms stable complexes with precious metals, intermediate to the chloride and cyanide complexes both of which have been shown sufficiently stable for industrial use.

Furthermore, plots of $\log\{[\text{Pt(II)}] \text{ or } [\text{Pt(IV)}]\}$ against $\log[\text{Pd(II)}]$ and $\log[\text{Pd(II)}]$ against $\log[\text{Ag(I)}]$ shown in Fig. 20A and B, suggested by Hancock et al. (1977), may be used to predict Pt and Pd values for which no experimental data are currently available in thiocyanate lixiviant systems. Fig. 20 shows a good linear correlation of the published values for all the ligands, displaying the validity of these constants. It is pertinent mentioning that the linear correlation of stability constants of complex species proposed by these authors paves the way to establish reliable thermodynamic data for Pt(II, IV) and Pd(II) complexes in thiocyanate solutions.

Elding (1978) has carried out extensive studies on Pt and Pd aqua complexes anation by Cl^- , Br^- , I^- and SCN^- . He observed

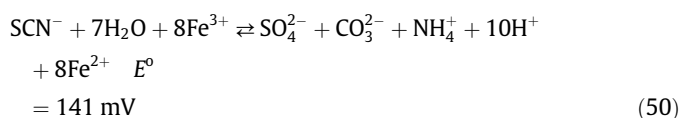
the following kinetic trans-effect order: $\text{H}_2\text{O} < \text{Cl}^- < \text{Br}^- < \text{I}^- < \text{SCN}^-$. Hence taking into account the differences in trans-effect between palladium and platinum, the former complexes react 5×10^5 times faster for all anation reactions and about 2×10^6 for all acid hydrolyses than the corresponding platinum complexes.

Platinum and palladium form a number of chloro complexes that have labile character towards several hydrophobic ligands such as SCN^- . This leads to the formation of several highly extractable complexes at room temperature (Fontas et al., 2009; Oleschuk and Chow, 1998). The SCN^- ligand can coordinate with either its 'hard' nitrogen atom, or 'softer' sulfur atom. Both platinum (IV) and palladium (II) form complexes coordinating with the sulfur atom, leading to $\text{Pt}(\text{SCN})_6^{2-}$ and $\text{Pd}(\text{SCN})_4^{2-}$ complexes formation according to reaction mechanisms in Eqs. (48) and (49), respectively (Oleschuk and Chow, 1998).



It is worth mentioning that palladium (II) in the presence of SCN^- undergoes a substitution reaction almost instantaneously in the form of $\text{Pd}(\text{SCN})_4^{2-}$, while platinum (IV) thiocyanate complex formation is highly dependent on SCN^- ; although its formation can be accelerated photochemically or with heating. The rate is also inversely proportional to pH and the reaction is completely inhibited at solution pH of 7 (Al-bazi and Chow, 1984). It would appear that in the absence of light and heat that palladium complex should still be formed. This observation has shed light on the expected differential PGM leaching rates.

4.3.3.3. Stability of SCN^- towards oxidation – PGM leaching kinetics. In gold leaching processes, the stability of thiocyanate species is strongly dependent on oxidation potential and leaching conditions (Li et al., 2012c). However, under the oxidation/leaching potentials required for gold dissolution, thiocyanate is thermodynamically unstable and can be oxidized by ferric ion to sulfate, carbonate and ammonium according to the reaction in Eq. (50) (Li et al., 2012a,c).



It is important to note that SCN^- oxidation occurs at a potential (141 mV) below that of the corresponding reaction for forming the precious metals complex, e.g. 691 mV for Au(I). Therefore, there is a competing reaction to gold dissolution which increases reagent consumption (Botz et al., 2001). Dunne et al. (2009) have indicated that thiocyanate is much more stable in the leaching of oxide ores than in the leaching of sulfide ores. Furthermore, Li et al. (2012c) have observed that thiocyanate oxidation by ferric ion in acidic solutions was slow at room temperature (25 °C) but significant at 50 °C. Conversely according to Barbosa and Monhemius quoted by Kuzugüdenli and Kantar (1999), for effective gold leaching,

conditions less desirable for safety and reagent stability (HSCN, pK_a at 25 °C equals 0.9), like low solution pH and very high temperature (85 °C) are required.

Besides being destroyed by oxidation during leaching, thiocyanate is known to form complexes with several metal cations. For example, a precipitate is formed with copper, probably as $\text{Cu}(\text{SCN})_2$, and the blood-red ferric-thiocyanate complexes are formed with iron. It should be noted that the formation of such stable compounds could reduce ferric ions oxidizing potential and the free thiocyanate concentration required for precious metals dissolution (Li et al., 2012a,b,c,d,e). While it may be possible to recirculate SCN^- in the iron complexes, the SCN^- in the precipitated copper complexes would be lost from the circuit. Thus it can be expected that this leaching system will suffer from significant reagent consumption (Adams, 2005; Aylmore, 2005).

Finally SCN^- gives a slow leaching rate. Li et al. (2012b) found that gold dissolution rate decreases with an increase in the leaching time. According to the authors, the slow gold dissolution rate which was almost insensitive to thiocyanate concentration and slightly dependent upon ferric ion concentration could be linked to the high anodic process overpotential for gold dissolution. They have suggested the use of catalysts in order to accelerate the rate and, at the same time, to reduce thiocyanate consumption (oxidation).

Yang et al. (2011) found that the addition of small amounts of thiourea to thiocyanate-ferric solutions had a synergistic effect on gold dissolution. The dissolution rate was found to be higher than that obtained when either ferric-thiocyanate or ferric-thiourea solutions were used separately at similar concentrations used in the mixture. In addition, the mixture has the advantage of being more stable towards oxidation in comparison with thiocyanate alone. The optimum concentration for thiourea and thiocyanate was about 0.005 M and 0.05 M, respectively.

4.3.3.4. Precious metals recovery from pregnant thiocyanate solutions. Recent research by Li et al. (2012d,e) considered and examined the three most common process strategies for gold recovery from pregnant thiocyanate solutions i.e., solvent extraction, cementation and activated carbon adsorption. Each method has its own advantages and disadvantages, and may be effective in recovering precious metals from the typical concentration of clear solutions, but may become less efficient or even inadequate when traces of precious metal ions are to be recovered from thiocyanate containing pulp (e.g., solvent extraction). No single industrial operation using PGM acid leaching in thiocyanate solutions has been reported.

5. Conclusions

During the last two decades, there have been great strides in new technology development for PGMs recovery from low-grade deposits. In attempting to summarize the large body of work, much detail has been sacrificed. It is hoped that the information provided will be sufficient to highlight some important issues relating to this matter and to point the reader in the direction of more detailed information, should this be required. The review has highlighted several areas worthy of special attention. These include the effects of salt additives, mechanical activation and redox potential control upon processes chemistry. Oxygen injection at supersonic velocity to overcome ferric regeneration inefficiency by oxygen/air use in atmospheric processing was also highlighted.

The apparent advantages and limitations in performance associated with each process have been discussed. By far, only four processes, namely Albion, Nitrogen Species Catalyzed (NSC), Outokumpu HydroCopper[®] and Total Pressure Oxidation, have

been commercially implemented on a large scale, basically for copper recovery except for the first two technologies which are treating precious metal containing feedstocks. However, each deposit's mineralogy poses its own challenges, particularly linked to mineral associations and the unique PGM make-up of each deposit. The complexity of PGM mineralogy (in particular when compared to gold) and the varied interactions of PGM minerals with lixiviants make for a complex metallurgical scenario where a-priori prediction of feasible processes is difficult.

In the Australian context, the Pantom Sill deposit contains PGM in various minerals including palladium antimonide (PdSb) and platinum arsenide (PtAs₂). The presence of base metal sulfides such as pentlandite (Ni,Fe)₉S₈, chalcocopyrite (CuFeS₂) and pyrite (FeS₂) have to be dealt with. Methods such as roasting and pressure leaching are capital intensive and, in the case of roasting, produce environmentally damaging emissions requiring management. The kinetics and acid leaching mechanisms of the above PGM-containing minerals vary and can be enhanced by modifying the leach conditions or by pre-treatment of the ores/concentrates (e.g., mechanical activation).

Acknowledgements

The authors would like to thank WASM (Western Australian School of Mines) for providing financial support for this project and the permission to publish this paper. Any opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of Curtin University.

References

- Adams, M.D., 2005. *Advances in Gold Ore Processing*, first ed. Wills, B.A., Netherlands.
- Adams, M., Lawrence, R., Bratty, M., 2008. Biogenic sulfide for cyanide recycle and copper recovery in gold–copper ore processing. *Miner. Eng.* 21 (6), 509–517.
- Adams, M., Liddell, K., Holohan, T., 2011. Hydrometallurgical processing of Platreef flotation concentrate. *Miner. Eng.* 24, 545–550.
- Afenya, P.M., 1991. Treatment of carbonaceous refractory gold ores. *Miner. Eng.* 4 (7–11), 1043–1055.
- Afolabi, A.S., Nkobane, M.P., Abdulkareem, A.S., 2012. Development of PGMs and chrome extraction circuit from UG-2 ore. In: *Proceedings of the World Congress on Engineering*, vol. 3.
- Aguilar, M., Farran, A., Marti, V., 1997. Capillary electrophoretic determination of cyanide leaching solutions from automobile catalytic converters. *J. Chromatogr. A* 778, 397–402.
- Al-bazi, S.J., Chow, A., 1984. Platinum metals-solution chemistry and separation methods (ion-exchange and solvent extraction). *Talanta* 31 (10A), 815–836.
- Anderson, C.G., 2003. Treatment of copper ores and concentrates with industrial nitrogen species catalyzed pressure leaching and non-cyanide precious metals recovery. *J. Miner., Met. Mater. Soc. (TMS)* 55, 32–36.
- AngloAmerican, 2011. *Building the Foundations for a Future through Mining. Integrated Annual Report*, 2011.
- Aylmore, M.G., 2005. Alternative lixiviants to cyanide for leaching gold ores. *Dev. Miner. Process.* 15, 501–539.
- Azaroual, M., Romand, B., Freyssinet, P., Disnar, J.R., 2001. Solubility of platinum in aqueous solutions at 25 °C and pHs 4 to 10 under oxidizing conditions. *Geochim. Cosmochim. Acta* 65 (24), 4453–4466.
- Baghalha, M., 2012. The leaching kinetics of an oxide gold ore with iodide/iodine solutions. *Hydrometallurgy* 113–114, 42–50.
- Balaz, P., Boldizarova, E., Achimovicova, M., Kammel, R., 2000. Leaching and dissolution of a pentlandite concentrate pretreated by mechanical activation. *Hydrometallurgy* 57, 85–96.
- Bax, A., 2004. Recovery of Platinum Group Metals. AP/P/2005/003433, Appl. 08/04/2004, Acc. 12/12/2008.
- Bax, A., Dunn, G.M., Lewins, D., 2009. Recovery of Platinum Group Metals. USA Patent 7,544,231 B2.
- Bezuidenhout, G.A., Davis, J., van Beek, B., Eksteen, J.J., 2012. Operation of a concentrated mode dual-alkali scrubber plant at the Lonmin smelter. *J. South. Afr. Inst. Min. Metall.* 112 (7), 657–665.
- Botz, M.M., Dimitriadis, D., Polglase, T., Phillips, W., Jenny, R., 2001. Processes for the regeneration of cyanide from thiocyanate. *Miner. Metall. Process.* 18 (3).
- Braemore resources Plc., 2009. *Annual Report & Consolidated Financial Statements for the Year Ended 30 June 2009*.
- Broadhurst, J.L., du Preez, J.G.H., 1993. A thermodynamic study of the dissolution of gold in an acidic aqueous thiocyanate medium using iron (III) sulfate as an oxidant. *Hydrometallurgy* 32, 317–344.
- Carneiro, M.F.C., Leão, V.A., 2007. The role of sodium chloride on surface properties of chalcocopyrite leached with ferric sulfate. *Hydrometallurgy* 87, 73–82.
- Chen, J., Huang, K., 2006. A new technique for extraction of platinum group metals by pressure cyanidation. *Hydrometallurgy* 82, 164–171.
- Cole, S., Joe Ferron, C., 2002. A Review of the Beneficiation and Extractive Metallurgy of the Platinum Group Elements, Highlighting Recent Process Innovations. SGS Minerals Services Technical Paper 2002-03.
- Córdoba, E.M., Muñoz, J.A., Blázquez, M.L., González, F., Ballester, A., 2008. Leaching of chalcocopyrite with ferric ion. Part III: effect of redox potential on the silver-catalyzed process. *Hydrometallurgy* 93, 97–105.
- Cramer, L.A., 2001. The extractive metallurgy of South Africa's platinum ores. *J. S. Afr. Inst. Min. Metall.* (October).
- Cyanide management, 2008. Department of Resources, Energy and Tourism. Australian Government.
- Dadgar, A., Howarth, J.N., Sergeant, R.H., Favstritsky, N.A., McKeown, J.A., Borden, D.W., Sanders, B.M., Likens, J., 1997. Inorganic Perbromide Compositions and Methods of Use Thereof. United States Patent Number 5,607,619.
- Dawson, R.J., Kelsall, G.H., 2007. Recovery of platinum group metals from secondary materials. I. Palladium dissolution in iodide solutions. *J. Appl. Electrochem.* 37, 3–14.
- Debernardi, G., Gentina, J.C., Albistur, P., Slanzi, G., 2013. Evaluation of processing options to avoid the passivation of chalcocopyrite. *Int. J. Miner. Process.* 125, 1–4.
- Deschenes, G., 2005. Advances in the cyanidation of gold. *Dev. Miner. Process.* 15, 479–500.
- Dixon, D.G., Tshilombo, A.F., 2005. Leaching Process for Copper Concentrates. United States Patent Application 2005/0269208 A1.
- Dreisinger, D., 2006. Copper leaching from primary sulfides: options for biological and chemical extraction of copper. *Hydrometallurgy* 83, 10–20.
- Dreisinger, D., 2012. Hydrometallurgical extraction of base, rare, and precious metals from complex and low grade resources. In: *XXVI International Mineral Processing Congress (IMPC) 2012 Proceedings/New Delhi, India/24–28 September 2012*.
- Dunne, R., Levier, M., Acar, S., Kappes, R., 2009. Keynote address: Newmont's contribution to gold technology. In: *World Gold Conference 2009, The Southern African Institute of Mining and Metallurgy*.
- Eksteen, J.J., 2011. A mechanistic model to predict matte temperatures during the smelting of UG2-rich blends of Platinum Group Metal concentrate. *Miner. Eng.* 24 (7), 676–687.
- Eksteen, J.J., Onyango, M.S., Pelsler, M., Lorenzen, L., Aldrich, C., Georgalli, G.A., 2008. Effects of residence time and mixing regimes on the precipitation characteristics of CaF₂ and MgF₂ from high ionic strength sulfate solutions. *Hydrometallurgy* 91 (1–4), 104–112.
- Eksteen, J.J., Bezuidenhout, G.A., van Beek, B., 2011. Cracking a hard nut: an overview of Lonmin's operations directed at smelting of UG2-rich concentrate blends. *J. South Afr. Inst. Min. Metall.* 111 (10), 681–690.
- Elding, L.L., 1978. Stabilities of platinum(II) chloro and bromo complexes and kinetics for anation of the tetraaquaplatinum(II) ion by halides and thiocyanate. *Inorg. Chim. Acta* 28, 255–262.
- Ellis, S., Mines, K.C.G., Kalsoorlie, W.A., 2008. Ultra Fine Grinding – A Practical Alternative to Oxidative Treatment of Refractory Gold Ores.
- Epstein, I.R., Kustin, K., Warshaw, L.J., 1980. A kinetics study of the oxidation of iron(II) by nitric acid. *J. Am. Chem. Soc.* 102 (11), 3751–3758.
- Fact Sheet, 2012. Platinum Group Metals. Polinares Working Paper 35 March 2012.
- Farinha, P.A., Correia, M.J.N., Carvalho, J.R., 1992. Technical note leaching of gold from a Portuguese concentrate with thiourea. *Miner. Eng.* 5 (8), 953–959.
- Ferron, C.J., Hamilton, C.C., Valeye, O., McKay, N., 2006. The Effect of the Mineralogy of the Platinum Group Metals on their Leachability During the Platsol[®] Leach Process. SGS Minerals Services Technical Paper 2006-03.
- Flatman, S., Battersby, R.M., Imhof, R., Battersby, R.M., Ibrayev, S., 2010. The Leachox[™] refractory gold process – the setting, design, installation and commissioning of a large scale plant at the Vasgold gold mine, Kazakhstan. *Precious Met.* 10.
- Fleming, C.A., 1992. Hydrometallurgy of precious metals recovery. *Hydrometallurgy* 30, 127–162.
- Fleming, C.A., 2002. Platsol[™] Process Provides a Viable Alternative to Smelting. SGS Minerals Services Technical Paper 2002-01.
- Fontas, C., Hidalgo, M., Salvado, V., 2009. Adsorption and preconcentration of Pd(II), Pt(IV), and Rh(III) using anion-exchange solid-phase extraction cartridges (SPE). *Solvent Extr. Ion Exch.* 27, 83–96.
- Geldenhuis, I.J., Jones, R.T., 2009. Four years of DC arc smelting of PGM-containing oxide feed materials at Mintek. In: *Nickel and Cobalt*, pp. 415–427.
- Georgalli, G.A., Eksteen, J.J., Onyango, M.S., Pelsler, M., Lorenzen, L., Aldrich, C., 2008. Fluoride based control of Ca and Mg concentrations in high ionic strength base metal sulfate solutions in hydrometallurgical circuits. *Miner. Eng.* 21 (3), 200–212.
- Gok, O., 2010. Oxidative leaching of sulfide ores with the participation of nitrogen species – a review. *J. Ore Dressing* 12 (24).
- Gok, O., Anderson, C.G., 2013. Dissolution of low-grade chalcocopyrite concentrate in acidified nitrite electrolyte. *Hydrometallurgy* 134–135, 40–46.
- Gok, O., Anderson, C.G., Cicekli, G., Cocen, E.I., 2013. Leaching kinetics of copper from chalcocopyrite concentrate in nitrous-sulfuric acid. *Physicochem. Problems Miner. Process.* 50 (1), 399–413.
- Gold Fields, 2013. <https://www.goldfields.co.za/gl_exp_arctic.php>.

- Green, B.R., Smit, D.M.C., Maumela, H., Coetzer, G., 2004. Leaching and recovery of platinum group metals from UG-2 concentrates. *J. S. Afr. Inst. Min. Metall.* (July)
- Grosse, A.C., Dicinovski, G.W., Shaw, M.J., Haddad, P.R., 2003. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy* 69, 1–21.
- Hamacek, J., Havel, J., 1999. Determination of platinum (II, IV) and palladium (II) as thiocyanate complexes by capillary zone electrophoresis analysis of carboplatin and similar drugs. *J. Chromatogr. A* 834, 321–327.
- Hancock, R.D., Finkelstein, N.P., Evers, A., 1977. A linear free-energy relation involving the formation constants of palladium (II) and platinum (II). *J. Inorg. Nucl. Chem.* 39, 1031–1034.
- Harjanto, S., Cao, Y., Shibayama, A., Naitoh, I., Nanami, T., Kasahara, K., Okumura, Y., Liu, K., Fujita, T., 2006. Leaching of Pt, Pd and Rh from automotive catalyst residue in various chloride based solutions. *Mater. Trans.* 47 (1), 129–135.
- Heinen, H.J., Peterson, D.G., Lindstrom, R.E., 1978. Processing Gold Ores Using Heap Leach-Carbon Adsorption Methods. United States Department of the Interior: Bureau of Mines Information Circular 8770.
- Hiroyoshi, N., Miiki, H., Hirajima, T., Tsunekawa, M., 2001. Enhancement of chalcopyrite leaching by ferrous ions in acidic ferric sulfate solutions. *Hydrometallurgy* 60, 185–197.
- Holtum, D.A., Murray, D.M., 1994. Bacterial heap leaching of refractory gold/sulfide ores. *Miner. Eng.* 7 (5–6), 619–631.
- Hourn, M.M., Rohner, P., Bartsch, P., Ngoviky, K., 2005. Benefits of using the Albion Process for a North Queensland Project and a Case Study of Capital and Operating Cost Benefits versus Bacterial Oxidation and Pressure Oxidation.
- Huang, K., Chen, J., Chen, Y.R., Zhao, J.C., Li, Q.W., Yang, Q.X., Zhang, Y., 2006. Enrichment of Platinum Group Metals (PGMs) by two-stage selective pressure leaching cementation from low-grade Pt–Pd sulfide concentrates. *Metall. Mater. Trans. B* 37B (October).
- Hyvärinen, O., Hämäläinen, M., Lamberg, P., Liipo, J., 2004. Recovering gold from copper concentrate via the HydroCopper™ process. *JOM* (August).
- Jeffrey, M., Anderson, C.G., 2003. A fundamental study of the alkaline sulfide leaching of gold. *Eur. J. Miner. Process. Environ. Prot.* (published in 2003)
- Jha, M.K., Lee, J.C., Kim, M.S., Jeong, J., Kim, B.S., Kumar, V., 2013. Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: a review. *Hydrometallurgy* 133, 23–32.
- Jones, R.T., 2002. ConRoast: DC arc smelting of dead-roasted sulfide concentrates. In: Stephens, R.L., Sohn, H.Y. (Eds.), *Sulfide Smelting*, Seattle, 17–21 February 2002, TMS (The Minerals, Metals & Materials Society).
- Jones, R.T., 2005. An overview of Southern African PGM smelting. In: *Nickel and Cobalt 2005: Challenges in Extraction and Production*, pp. 147–178.
- Jones, R.T., 2009. Towards commercialisation of Mintek's ConRoast process for platinum smelting. In: *Nickel and Cobalt 2009: Advances in the Processing of Nickel, Cobalt and PGMs using Pyrometallurgical Techniques*, 48th Annual Conference of Metallurgists, pp. 159–168.
- Kerley, B.J., 1983. Recovery of Precious Metals from Difficult Ores. U.S. Patent 4,369,061.
- Koek, M., Kreuzer, O.P., Maier, W.D., Porwal, A.K., Thompson, M., Guj, P., 2010. A review of the PGM industry, deposit models and exploration practices: implications for Australia's PGM potential. *Resour. Policy* 35, 20–35.
- Korte, F., Spittler, M., Coulston, F., 2000. The cyanide leaching gold recovery process is a unsustainable technology with unacceptable impacts on ecosystems and humans: the disaster in Romania. *Ecotoxicol. Environ. Saf.* 46 (3), 241–245.
- Kowalczyk, P., Chmielewski, T., 2008. Search for a New Technology Producing Copper from Chalcopyrite. *Scientific Papers of the Institute of Mining*, No 122, Conferences No 51, 7th PhD Studies Scientific Conference, Interdisciplinary Topics in Mining and Geology, Ofic. Wyd. PWR., Wrocław, 94–100.
- Kriek, R.J., 2008. Leaching of Selected PGMs: A Thermodynamic and Electrochemical Study Employing Less Aggressive Lixiviants. MSc Thesis, University of Cape Town.
- Kuzugüdenli, Ö.E., Kantar, Ç., 1999. Alternates to gold recovery by cyanide leaching. *Erciyes Üniversitesi Fen Bilimleri Dergisi* 15 (1–2), 119–127.
- Kyriakakis, G., 2005. Extraction of gold from platinum group metal (PGM) ores. *Dev. Miner. Process.* 15, 897–917.
- La Brooy, S.R., Linge, H.G., Walker, G.S., 1994. Review of gold extraction from ores. *Miner. Eng.* 7 (10), 1213–1241.
- Lewins, J., 2006. Platinum service. *Mater. World* (January), 30–32.
- Lewins, J., Greenaway, T., 2004. The Pantan Platinum–Palladium Project. The Australian Institute of Mining and Metallurgy Bulletin, July–August 04.
- Li, J., Miller, J.D., 2006. A review of gold leaching in acid thiourea solutions. *Miner. Process. Extr. Metall. Rev.* 27, 177–214.
- Li, J., Wan, R.Y., LeVier, K.M., Miller, J.D., 2008. Thiocyanate process chemistry for gold recovery. In: Young, C.A., Taylor, P.R., Anderson, C.G., Choi, Y. (Eds.), *Hydrometallurgy 2008, Proceedings of the Sixth International Symposium*. Phoenix, AZ, USA, pp. 824–836.
- Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012a. Thiocyanate hydrometallurgy for the recovery of gold. Part I: chemical and thermodynamic considerations. *Hydrometallurgy* 113–114, 1–9.
- Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012b. Thiocyanate hydrometallurgy for the recovery of gold. Part II: the leaching kinetics. *Hydrometallurgy* 113–114, 10–18.
- Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012c. Thiocyanate hydrometallurgy for the recovery of gold Part III: thiocyanate stability. *Hydrometallurgy* 113–114, 19–24.
- Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012d. Thiocyanate hydrometallurgy for the recovery of gold. Part IV: solvent extraction of gold with Alamine 336. *Hydrometallurgy* 113–114, 25–30.
- Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012e. Thiocyanate hydrometallurgy for the recovery of gold. Part V: process alternatives for solution concentration and purification. *Hydrometallurgy* 113–114, 31–38.
- Li, Y., Kawashima, N., Li, J., Chandra, A.P., Gerson, A.R., 2013. A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. *Adv. Colloid Interface Sci.* 197–198, 1–32.
- Liddell, K.S., Adams, M.D., 2012. Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates. *J. South. Afr. Inst. Min. Metall.*, 112
- Liddell, K., Newton, T., Adams, M., Muller, B., 2010. Energy consumptions for Kell hydrometallurgical refining versus conventional pyrometallurgical smelting and refining of PGM concentrates. In: *The 4th International Platinum Conference, Platinum in Transition 'Boom or Bust', The Southern African Institute of Mining and Metallurgy*.
- Lorenzen, L., van Deventer, J.S.J., 1992. The mechanism of leaching of gold from refractory ores. *Miner. Eng.* 5 (10–12), 1377–1387.
- Lorenzen, L., Eksteen, J.J., Pelsler, M., Aldrich, C., Georgalli, G., 2009. Activated alumina-based adsorption and recovery of excess fluoride ions subsequent to calcium and magnesium removal in base metal leach circuits. *J. S. Afr. Inst. Min. Metall.* 109 (8), 447–453.
- Lu, Z.Y., Jeffrey, M.I., Lawson, F., 2000. The effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy* 56, 189–202.
- Lundström, M., 2009. Chalcopyrite Dissolution in Cupric Chloride Solutions. PhD Thesis, Helsinki University of Technology.
- Lundström, M., Aromaa, J., Forsen, O., Hyvarinen, O., Barker, M.H., 2005. Leaching of chalcopyrite in cupric chloride solution. *Hydrometallurgy* 77, 89–95.
- Lundström, M., Aromaa, J., Forsen, O., Hyvarinen, O., Barker, M.H., 2007. Cathodic reactions of Cu²⁺ in cupric chloride solution. *Hydrometallurgy* 85, 9–16.
- Lundström, M., Aromaa, J., Forsen, O., 2009. Redox potential characteristics of cupric chloride solutions. *Hydrometallurgy* 95, 285–289.
- Mahmoud, M.H.H., 2003. Leaching platinum-group metals in a sulfuric acid/chloride solution. *JOM* (April).
- Marsden, J.O., Brewer, R.E., Hazen, N., 2003. Copper concentrate leaching developments by Phelps dodge corporation. In: Young, C.A., Alftmtazi, A.M., Anderson, C.G., Dreisinger, D.B., Harris, B., James, A. (Eds.), *Hydrometallurgy 2003 – Fifth International Conference in Honour of Professor Ian Ritchie: Electrometallurgy and Environmental Hydrometallurgy*, vol. 2, TMS (The Minerals, Metals & Materials Society).
- Mateos, F.B., Perez, I.P., Mora, F.C., 1987. The passivation of chalcopyrite subjected to ferric sulfate leaching and its reactivation with metal sulfides. *Hydrometallurgy* 19, 159–167.
- Maurice, D., Hawk, J.A., 1999. Ferric chloride leaching of a mechanically activated pentlandite–chalcopyrite concentrate. *Hydrometallurgy* 52, 289–312.
- McInnes, C.M., Sparrow, G.J., Woodcock, J.T., 1994. Extraction of platinum, palladium and gold by cyanidation of Coronation Hill ore. *Hydrometallurgy* 35, 141–159.
- Meersbergen, M.T., Lorenzen, L., Deventer, J.S.J., 1993. The electrochemical dissolution of gold in bromine medium. *Miner. Eng.* 6 (8–10), 1067–1079.
- Miezitis, Y., 2014. Australia's Identified Mineral Resources 2013. Commonwealth of Australia (Geoscience Australia) 2014. ISSN: 1327-1466.
- Milbourne, J., Tomlinson, M., Gormely, L., 2003. Use of hydrometallurgy in direct processing of base metal/PGM concentrates. *Hydrometallurgy*, 625.
- Mountain, B.W., Wood, S.A., 1988. Chemical controls on the solubility, transport, and decomposition of platinum and palladium in hydrothermal solutions: a thermodynamic approach. *Econ. Geol.* 83, 492–510.
- Moyes, J., Crescent, M., 1999. The INTEC copper process. *Copper*.
- Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2014. Evaluation of the Merrill-Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solutions. *Hydrometallurgy* 142, 36–46.
- Muir, D.M., Ariti, J., 1991. Studies on the dissolution of platinum and palladium from low grade ores and by-products. In: *Extractive Metallurgy Conference*, Perth, 2–4 October 1991.
- Munoz, G.A., Miller, J.D., 1999. Noncyanide Leaching of an Auriferous Pyrite Ore from Ecuador. For Presentation at the Society for Mining, Metallurgy, and Exploration, Inc., Annual Meeting Denver, Colorado, March 1–3, 1999.
- Mwase, J., 2009. Hydrometallurgical Extraction of Platinum Group Metals from a Low-Grade Ore Concentrate. MSc Thesis, University of Cape Town.
- Mwase, J.M., Petersen, J., Eksteen, J.J., 2012a. Assessing a two-stage heap leaching process for Platreef flotation concentrate. *Hydrometallurgy* 129–130, 74–81.
- Mwase, J.M., Petersen, J., Eksteen, J.J., 2012b. A conceptual flowsheet for heap leaching of platinum group metals (PGMs) from a low-grade ore concentrate. *Hydrometallurgy* 111–112, 129–135.
- Mwase, J.M., Petersen, J., Eksteen, J.J., 2014. A novel sequential heap leach process for treating crushed Platreef ore. *Hydrometallurgy* 141, 97–104.
- Nazari, G.T., 2012. Enhancing the Kinetics of Pyrite Catalyzed Leaching of Chalcopyrite. PhD Thesis, University of British Columbia.
- Nazari, G., Asselin, E., 2009. Morphology of chalcopyrite leaching in acidic ferric sulfate media. *Hydrometallurgy* 96, 183–188.
- Nazari, G., Dixon, D.G., Dreisinger, D.B., 2011. Enhancing the kinetics of chalcopyrite leaching in the Galvanox™ process. *Hydrometallurgy* 105, 251–258.

- Nazari, G., Dixon, D.G., Dreisinger, D.B., 2012a. The role of galena associated with silver-enhanced pyrite in the kinetics of chalcopyrite leaching during the Galvanox™ process. *Hydrometallurgy* 113–114, 177–184.
- Nazari, G., Dixon, D.G., Dreisinger, D.B., 2012b. The role of silver-enhanced pyrite in enhancing the electrical conductivity of sulfur product layer during chalcopyrite leaching in the Galvanox™ process. *Hydrometallurgy* 111–112, 35–45.
- Nazari, G., Dixon, D.G., Dreisinger, D.B., 2012c. The mechanism of chalcopyrite leaching in the presence of silver-enhanced pyrite in the Galvanox™ process. *Hydrometallurgy* 113–114, 122–130.
- Oleschuk, R.D., Chow, A., 1998. The separation of platinum and palladium by selective extraction of $H_2Pt(SCN)_6$ and $H_2Pd(SCN)_4$ using a polyTHF-impregnated filter. *Talanta* 45 (6), 1235–1245.
- Oraby, E., Eksteen, J.J., 2013. A Process of Precious Metals Recovery. Australian Provisional Patent Application No 2,013,903,380.
- Oraby, E.A., Eksteen, J.J., 2014. The selective leaching of copper from a gold–copper concentrate in glycine solutions. *Hydrometallurgy* 50, 14–19.
- Palmer, C.M., Johnson, G.D., 2005. The Activox® process: growing significance in the nickel industry. *JOM* (July).
- Phillips, R.E., Jones, R.T., Chennells, P., 2008. Commercialization of the ConRoast process. In: Third International Platinum Conference ‘Platinum in Transformation’, The Southern African Institute of Mining and Metallurgy.
- Prasad, M.S., Mensah-Biney, R., Pizarro, R.S., 1991. Modern trends in gold processing – overview. *Miner. Eng.* 4 (12), 1257–1277.
- Pugaev, D., Nicol, M., Senanayake, G., 2011. The mechanisms of the passivation of sulfide minerals in oxidative leaching processes. In: 6th Southern African Base Metals Conference, The Southern African Institute of Mining and Metallurgy, 2011.
- Ritchie, S., Eksteen, J.J., 2011. Investigating the effect of slag bath conditions on the existence of “mushy” zones in PGM smelting furnaces using computational fluid dynamics. *Miner. Eng.* 24 (7), 661–675.
- Rosia Montana Gold Corporation S.A., 2007. Flowsheet and Leaching Alternatives for the Rosia Montana Flowsheet. Processing and Leaching Alternatives.
- Saari, T., 2005. Platinum Exploration and Mining in Finland – An Overview. Invest in Finland, Aleksanterinkatu 17 P.O. Box 800, FIN-00101 Helsinki, Finland.
- Sammot, D., Welham, N.J., 2002. The Intec copper process: a detailed environmental analysis. In: Green Processing Conference, 29–31 May 2002.
- Sanders, J.F., 1926. Process of Extracting Arsenide from Ores. United States Patent 1,581,475.
- Schoeman, E., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., 2012. The Recovery of Platinum, Palladium, and Gold from a Cyanide Heap Solution, with Use of Ion Exchange Resins. The Southern African Institute of Mining and Metallurgy Platinum.
- Senanayake, G., 2004a. Fundamentals and applications of metal–ligand complexes of gold(I/III) in non-cyanide gold processes. In: Green Processing Conference Fremantle, WA, 10–12 May 2004.
- Senanayake, G., 2004b. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications. *Miner. Eng.* 17, 785–801.
- Senanayake, G., 2009. A review of chloride assisted copper sulfide leaching by oxygenated sulfuric acid and mechanistic considerations. *Hydrometallurgy* 98, 21–32.
- Snyders, C.A., Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., 2012. The Adsorption and Elution of Platinum Group Metals (Pt, Pd, and Au) from Cyanide Leach Solutions using Activated Carbon. The Southern African Institute of Mining and Metallurgy Platinum.
- Snyders, C.A., Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., 2013. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions. *J. South. Afr. Inst. Min. Metall.* 113.
- Sparrow, G.J., Woodcock, J.T., 1995. Cyanide and other lixiviant leaching systems for gold with some practical applications. *Miner. Process. Extract. Metall. Rev.: Int. J.* 14, 193–247.
- Staunton, W.P., 2005. Carbon-in-pulp. *Dev. Miner. Process.* 15, 562–587.
- Tatarnikov, A.V., Sokolskaya, I., Shneerson, Y.M., Lapin, A.Y., Goncharov, P.M., 2004. Treatment of platinum flotation products. *Platin. Met. Rev.* 48 (3), 125–132.
- Trexler, D.T., Flynn, T., Hendrix, J.L., 1990. Heap leaching. *Geo-Heat Center Bull.* (Summer).
- Trickey, S., 2010. Options for PGM supply outside of Africa. In: The 4th International Platinum Conference, Platinum in Transition ‘Boom or Bust’, The Southern African Institute of Mining and Metallurgy.
- Turkmen, Y., Kaya, E., 2009. Acidified ferric chloride leaching of a chalcopyrite concentrate. *J. Ore Dressing* 11 (22).
- Turner, D.W., Hourn, M., 2013. Albion Process Simplicity in Leaching: Copper Applications. Xstrata Technology.
- Vukcevic, S., 1996. A comparison of alkali and acid methods for the extraction of gold from low grade ores. *Miner. Eng.* 9 (10), 1033–1047.
- Wan, R.Y., LeVier, K.M., 2011. Precious Metal Recovery using Thiocyanate Lixiviant. US Patent 7,947,108 B2.
- Wan, R.Y., LeVier, M., Miller, J.D., 1993. Research and development activities for the recovery of gold from noncyanide solutions. In: Hisky, J.B., Warren, G.W. (Eds.), *Hydrometallurgy Fundamentals, Technology and Innovation*, pp. 415–436.
- Wang, S., 2005. Copper leaching from chalcopyrite concentrates. *JOM* (July).
- Wilburn, D.R., 2012. Global Exploration and Production Capacity for Platinum-Group Metals from 1995 through 2015.
- Wilburn, D.R., Bleiwas, D.I., 2004. Platinum-Group Metals-World Supply and Demand. U.S. Geological Survey Open-File Report 2004-1224.
- Winand, R., 1991. Chloride hydrometallurgy. *Hydrometallurgy* 27, 285–316.
- WPIC., 2014. The World Platinum Investment Council. Press Release. London, 03 December 2014.
- Xiao, Z., Laplante, A.R., 2004. Characterizing and recovering the platinum group Minerals – a review. *Miner. Eng.* 17, 961–979.
- Yang, X., Shi, X., Xu, H., Moats, M.S., Miller, J.D., Xiao, X., Ma, L., 2011. Leaching of gold in acid thiourea-thiocyanate solutions using ferric sulfate as oxidant. In: TMS 2011 140th Annual Meeting and Exhibition, Materials Processing and Energy Materials, vol. 1. John Wiley & Sons, p. 299.
- Zanjani, A., Baghalha, M., 2009. Factors affecting platinum extraction from used reforming catalysts in iodine solutions at temperatures up to 95 °C. *Hydrometallurgy* 97, 119–125.
- Zhang, Y., Liu, S., Xie, H., Zeng, X., Li, J., 2012. Current status on leaching precious metals from waste printed circuit boards. *Proc. Environ. Sci.* 16, 560–568.

CHAPTER III : SULFURIC ACID BAKE PROCESS AT 550°C

Submitted for publication as

Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore.

Cleoplace Ngoie Mpinga, Jacques Eksteen, Chris Aldrich, Laurence Dyer., 2017.
Minerals Engineering 110, 153-165.

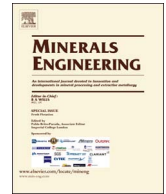
Accepted for publication on 27th April 2017.

© 2017 Elsevier Ltd.

Reprinted with permission from the publisher.

SUMMARY

Chapter III focuses solely on sulfation roast at 550°C, which is the highest temperature in the “Panton process”. Outcomes at said temperature are interpreted and discussed. Sperrylite behaviours after roasting and leaching are highlighted. Emphasis was placed on platinum due to its reputation of being more refractory towards oxidation/dissolution in comparison with palladium.



Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore



Cleophae Ngoie Mpinga, Jacques Eksteen*, Chris Aldrich, Laurence Dyer

Department of Mining Engineering and Metallurgical Engineering, Western Australian School of Mines, Curtin University, GPO Box U1987, Perth 6845, Western Australia, Australia

ARTICLE INFO

Keywords:

Cu leaching
Ni leaching
Sulfation roast
PGM ore
Response surface methodology
Chromitite

ABSTRACT

Selective sulfation-roast-water leach process of a complex, chromite-rich Cu-Ni-PGM ore to dissolve water-soluble base metal sulfates contained therein was investigated as an alternative process to remove base metals prior to the extraction of precious metals. Ground run-of-mine ore ($P_{80} < 75 \mu\text{m}$) was mixed with concentrated H_2SO_4 (sulfating agent) and Na_2SO_4 (dual catalyst and sulfating agent) to intensify atmospheric sulfation roast reaction in an unvented electric furnace (static roast under reducing conditions). The acquired calcine was water leached to extract the Ni and Cu sulfates. The roasting conditions were optimized using a Response Surface Methodology which included a Desirability Function Approach in order to maximize Cu and Ni extraction whilst limiting reagent consumption and suppressing Fe and Cr co-dissolution.

It was possible to decompose the chromatic-ferritic structure and produce water-soluble metal species by roasting the ore containing 12.80 g/t Pt, 15.20 g/t Pd, 0.0646% Cu, 0.31% Ni, 13.60% Fe and 10.40% Cr. Approximately 90% Ni and 77% Cu were recovered after roasting at 550 °C in closed atmosphere for 2 h with 462 kg/t H_2SO_4 , 76.9 kg/t Na_2SO_4 and by leaching at 80 °C with 2 wt% solid density for 24 h. The raw ore, roasted mass and water-leach residue were characterized by fire assay and Tescan Integrated Mineral Analysis (TIMA GM Model). Pt + Pd grade has been upgraded from 28 (raw ore) to 32.38 g/t (water-leach residue).

1. Introduction

The Pantong Sill is a chromite rich ore body bearing economic grades of Platinum Group Metals (PGMs) and high nuisance levels of Ni and Cu. It is a remote deposit situated in the Kimberly region of Western Australia. A process was developed that used roasting and hydrometallurgical techniques to extract the metal values (Bax et al., 2009). For the purposes of further reference this process will be referred to as the “Pantong process” which has been described at high level by Lewins and Greenaway (2004). The Pantong Process proposes a complex recovery route using a combination of Calcination Cyanidation — Low pH precipitation and Acid pressure oxidative leach.

However, the overall process suffers from some shortcomings such as long leaching time (slow leaching rate), unexplained precipitation and redissolution steps, large reagent consumption (due to reacting base metal sulfides), loss of platinum to tailings, and an inherently complex flowsheet. As a result, alternative hydrometallurgical and/or hybrid pyro-hydrometallurgical routes are considered. Mpinga et al. have reviewed various non-smelting process options and have shown the potential of various hydrometallurgical option, which may or may

not include a roasting step (Mpinga et al., 2015, 2014a,b).

Leaching tests were performed to determine feasible means of extracting copper and nickel values (the latter being the most valuable base metal) and simultaneously concentrating platinum metals in a solid residue. As these metals are also significant reagent consumers during the precious metal leach stages, it is worthwhile to remove them as completely as economically possible prior to precious metals extraction. Note that previous studies have shown the refractoriness of the ore to direct cyanide leaching even after fine grinding (Lewins and Greenaway, 2004). Accordingly, it is essential to pretreat the ore by roasting, pressure oxidation, bio- or chemical oxidation, or mechanical activation to oxidize/disintegrate the sulfide matrix and further remove these reagent consuming species prior to PGM extraction (Ellis, 2003; Senanayake, 2004; Prasad et al., 1991).

The selection of the optimal method is based on economic evaluation and depends greatly on location and legislative controls. By way of example, within Australia, the National Health and Medical Research Council (NHMRC) has developed a set of limits for some of the major air pollutants based on their effect on human health, including a 10 min sulfur dioxide goal of 0.25 ppm (NEPC, 2004). The roasting pretreat-

* Corresponding author.

E-mail address: jacques.eksteen@curtin.edu.au (J. Eksteen).

<http://dx.doi.org/10.1016/j.mineng.2017.04.019>

Received 9 February 2017; Received in revised form 26 April 2017; Accepted 27 April 2017

Available online 08 May 2017

0892-6875/ © 2017 Elsevier Ltd. All rights reserved.

ment technique was chosen as it has been proposed for the Panton process. La Brooy et al. (1994) pointed out that roasting without sulfur dioxide recovery (emission) is one of the most cost-effective processing options for low sulfur orebodies in remote locations. Current environmental legislation would normally require an alkaline scrubbing system. It should be apparent that the material under investigation is an ideal candidate for a roasting process, owing to its low total sulfur content of 0.78%.

The objective of the present work was to determine whether the introduction of a sulfation roast pretreatment step (instead of conventional oxidation roasting) to break down the crystal lattices, thereby rendering copper and nickel containing phases amenable to water leaching, would result in their recoveries and simultaneously concentrating platinum metals in a solid residue. The effects of H₂SO₄ (sulfating agent), Na₂SO₄ (catalyst), roasting temperature, roasting time, leaching temperature, oxygen addition at the leaching stage and leaching duration on the dissolution efficiency of various metals including iron, chromium and PGMs were explored with the aim of minimizing them; keeping in mind that the ore under examination contains a large amount (78.12%) of chromite gangue, FeCr₂O₄.

2. Theoretical background

2.1. Current practice—Pyrometallurgical approaches

The ore that is best known and similar to the Panton ore in terms of chromite content is the Upper Group 2 (UG-2) ore as found in the Bushveld Igneous Complex in South Africa. The processing of high chromite content ores UG-2 was pioneered by Lonmin Plc. in the 1980s (Jones, 2005). Lonmin Plc. is the world's third largest primary platinum producer after Anglo Platinum and Impala Platinum (Wilburn, 2012). The predominant portion of Lonmin's current annual PGM production is sourced from the UG-2 (Jones, 2005). As a consequence, Lonmin Plc. has developed and patented an integrated hydrometallurgical method, suitable for economically treating low-grade PGM sulfide concentrates with large amounts of chromite gangue (Bax et al., 2009). However, the process still involves the controversial cyanide leaching technique with its inherent health hazards, which causes a high environmental liability, as well as additional expenses related to legal and safe disposal.

Various attempts at treating these PGM-bearing chromite ores have also been described by other workers. These include work by Liddell and Adams (2012) and Liddell et al. (2011) that involves the roasting of a residue from sulfidic pressure oxidation at 900 °C, and subsequent atmospheric leaching of the precious metals in chloride media, as typically used in PGM refineries. Green et al. (2004) have proposed a hydrometallurgical process that comprises a reductive roast at ≥800 °C, followed by the leaching of the products in HCl/chlorine solutions.

Another alternative approach has been jointly developed between Mintek and Falconbridge: the ConRoast process (Jones, 2005). The technology is based on a complete sulfur removal by dead-roasting at around 950 °C, followed by the smelting of the dead-roasted concentrate in a DC arc furnace at about 1585 °C. The ConRoast process uses an iron-based alloy as a collector for nickel, copper, cobalt and PGMs (Jones, 2002). The energy intensive nature of these processes generally limits their application to higher grade concentrates rather than whole ores.

2.2. Potential approaches—Hybrid pyro-hydrometallurgical options

2.2.1. Panton process

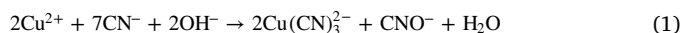
The hybrid pyro-hydrometallurgical work (Fig. 1) by Platinum Australia Limited (PLA) on Panton concentrates (P₈₀ of 38 μm) showed that atmospheric cyanide leaching—following a low-temperature calcination step—could only recover up to 86% Pd, 99% Au, but less than 10% Pt. Fine grinding to P₈₀ of 14 μm provided merely small improvement (Lewins and Greenaway, 2004).

The retention time of a leaching circuit is important for the

performance of any plant, because longer extraction time means lower efficiency of equipment utilization. The long cyanidation retention time of 100 h (Fig. 1) is uncommon in practice, especially after calcination pretreatment stage of the concentrates. This requires much larger tanks (capital cost). For instance in the cyanidation process of gold, the solid matter is often treated with a diluted solution of NaCN for typical residence times ranging from 20 to 40 h depending on the head grade and nature of the ore (Stange, 1999).

Even though the Panton process suggested a low temperature cyanidation, Sibrell et al. (1994) have shown that the kinetics of PGM leaching is significantly accelerated using elevated temperatures and pressures. Furthermore, copper and nickel are strong cyanicides, as they consume cyanide reagent potentially to the point of rendering a process uneconomical (Mpinga et al., 2014a; Brierley and Brierley, 2001). Muir (2011) stated that copper minerals consume approximately 30 kg NaCN per ton of ore for every 1% of reactive Cu present or about 2.3 kg of NaCN for every kilogram of Cu leached. Sceresini (2005) stated that the cyanidation of Cu(II) minerals with the consequent formation of cyanogen, (CN)₂, can result in the loss of cyanide in the proportion of 0.39 kg NaCN/kg Cu(II) leached.

The presence of cupric copper in an ore results in the irreversible loss of cyanide as cyanate according to the reaction in Eq. (1) (Breuer et al., 2009; Sceresini, 2005). The calcination carried out according to the process shown in Fig. 1 promotes the oxidation of all copper minerals present in the feed material. This renders them more amenable to cyanide leaching, and increases the lixiviant and oxygen consumptions. In addition, the generation of Cu(CN)₃²⁻ is also a significant problem, because its presence in tailings supernatant tends to stabilize weak-acid dissociable cyanide in a form toxic to wildlife yet less amenable to natural degradation processes (Lawrence and López, 2011). The Panton process suffers also from the discharge of slow-dissolving platinum minerals, such as sperrylite, to tailings storage facilities.



2.2.2. Selective sulfation roast processes

Owing to the more stringent environmental regulations, as well as the need to reduce energy consumption, metals production by sulfation roasting is gaining more attention as an alternative process to smelting (Yu et al., 2012; Prasad and Pandey, 1998; Norrgran, 1985). The method is advantageous as it decomposes the components of a material at moderate temperatures, with their conversion to water-soluble sulfates and thereby simultaneous concentrate platinum metals in a solid residue (Dimitrijevic et al., 2016; Kshumaneva et al., 2014).

The sulfation roast process can be carried out by a number of sulfate promoters, such as H₂S, H₂SO₄, (NH₄)₂SO₄, Fe₂(SO₄)₃·H₂O, FeS₂, KOH, NaOH, K₂SO₄, Na₂SO₄, Na₂CO₃, etc. (Parirenyatwa et al., 2016; Yu et al., 2014a,b; Hunt and Kraus, 2013; Guo et al., 2012, 2009; Frankiewicz, 1978). Frankiewicz (1978) found that the salt to concentrate ratio affected the conversion of both copper and nickel with the larger effect being on nickel conversion. Generally, the mass ratio should lie within the 0.05–0.50 range, and the higher the ratio, the higher the degree of conversion. The preferred reactor for sulfation roast processes is the fluidized bed roaster (Hanf and Schmidt, 1979).

2.2.2.1. Predicting prevailing phase equilibria at the roasting stage.

Graphically, roasting thermodynamics can be expressed by predominance area diagrams, or Kellogg diagrams. Representative Kellogg diagrams drawn at 550 °C using the HSC Chemistry® 7.1 software package are shown in Fig. 2. In general, the increase of both sulfur dioxide and oxygen partial pressures enhances the formation of sulfates at a given temperature (Safarzadeh et al., 2014).

The formation of CuSO₄ and NiSO₄ are thermodynamically feasible at 550 °C. The optimal conditions (partial pressures) can be estimated by superimposing—at same scale—the above stability diagrams as

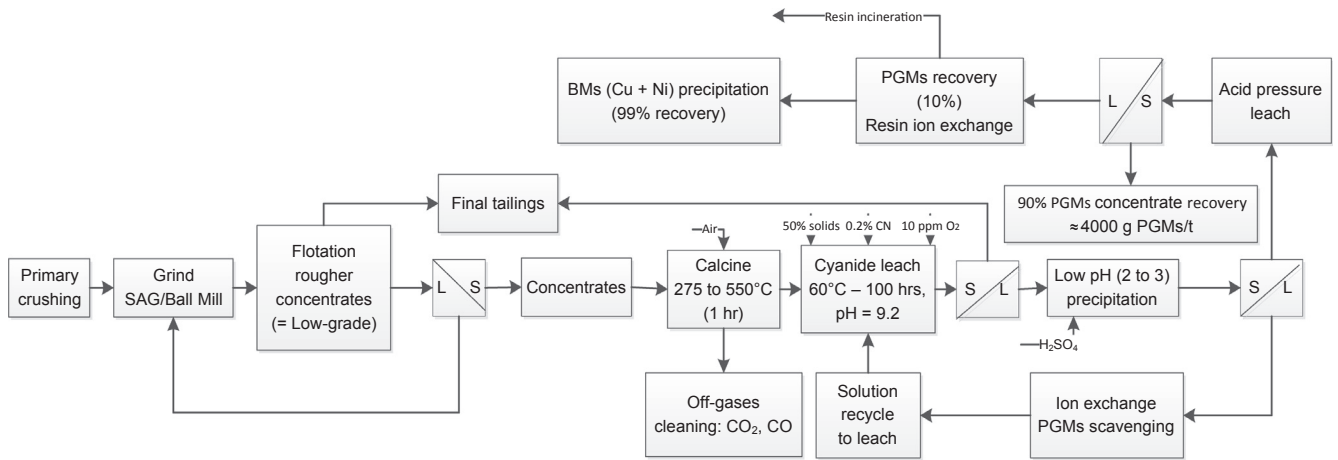


Fig. 1. Panton process conceptual flow schematic (Lewins and Greenaway, 2004).

shown in Fig. 3. It is essential to be aware that the complex systems encountered in practice involve numerous interactions (e.g., presence of catalysts and/or sulfating agents) which may greatly alter the simple sulfation equilibria (Kellogg, 1964). In addition, the software package uses pure substances to calculate thermodynamic properties.

The roasting process can dramatically improve base metals leaching rate. However, it may also form secondary wrapping (e.g. metal ferrites, FeAsO₄, etc.) that can reduce the leaching rate of forthcoming PGMs. Although the mechanisms that retain arsenic in calcines are complicated and still poorly understood (Walker et al., 2015), several studies

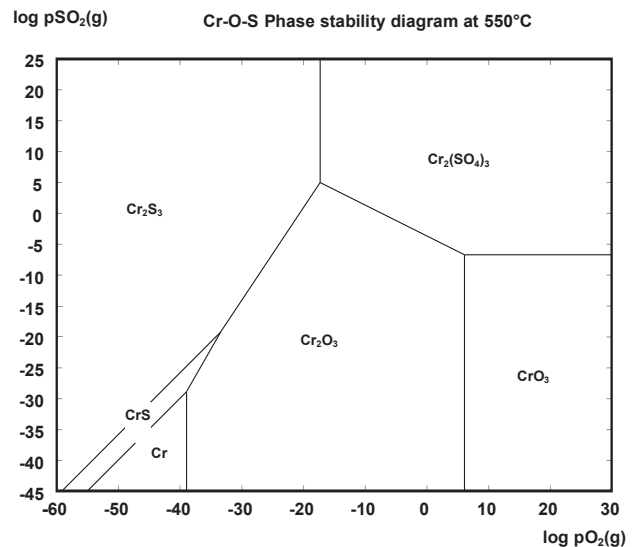
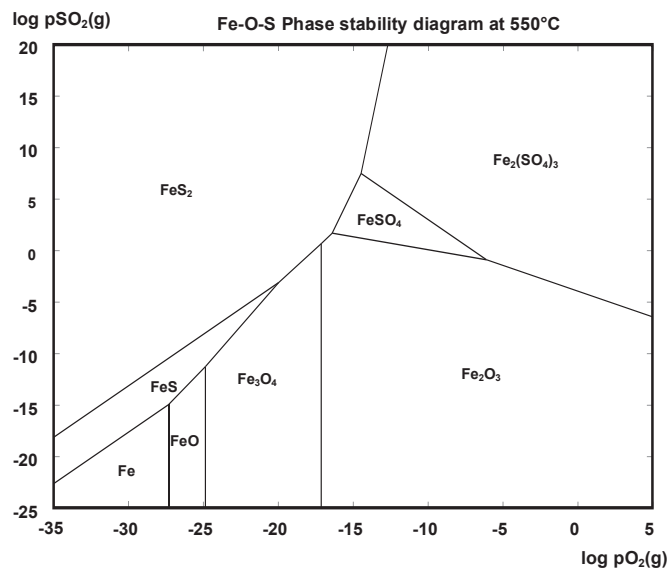
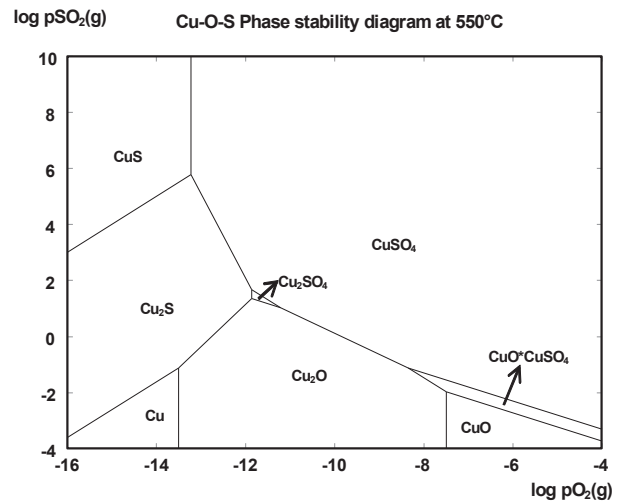
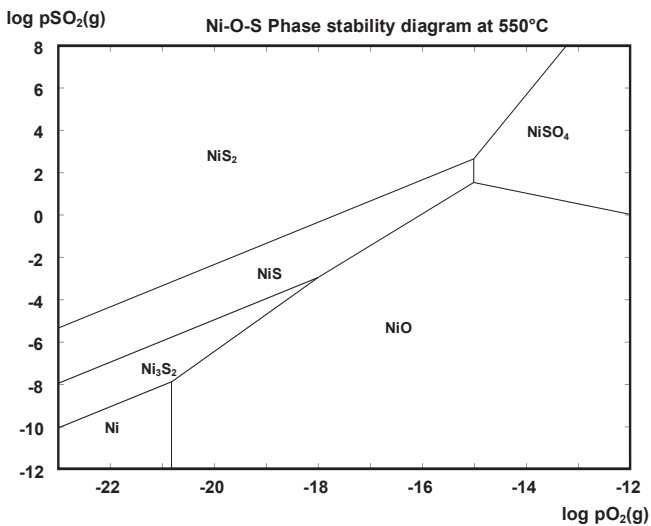


Fig. 2. Me-O-S phase stability diagrams drawn at 550 °C using the HSC Chemistry® 7.1 software package. Me denotes Ni, Cu, Fe and Cr.

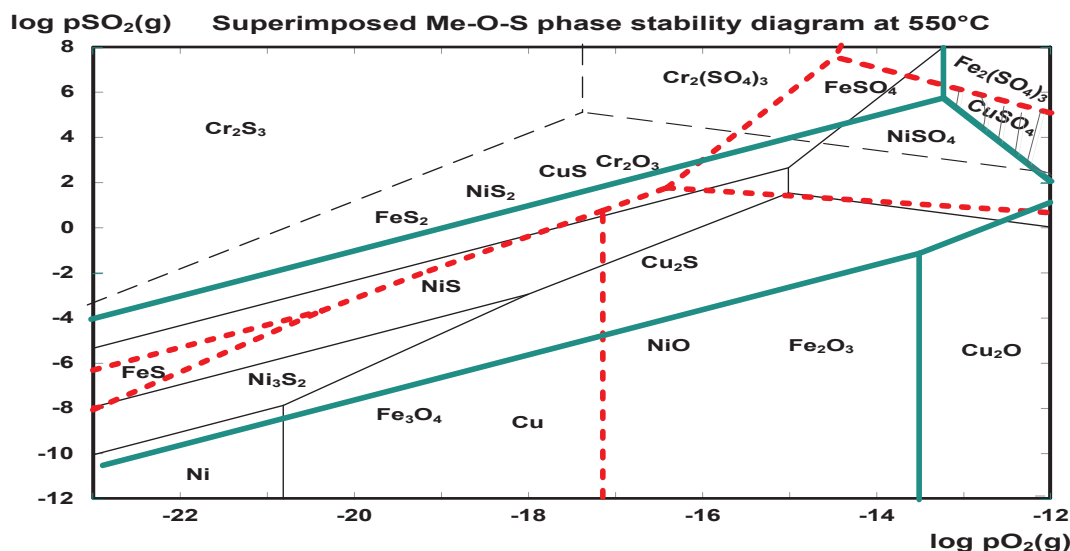


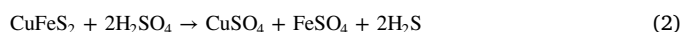
Fig. 3. Superimposed predominance area diagrams for Ni-O-S (thin solid lines), Cu-O-S (thick solid lines), Cr-O-S (thin broken lines) and Fe-O-S (thick broken lines) at 550 °C.

have revealed its tendency to be retained in calcines during the roasting of arsenic-bearing sulfides. This may be elucidated by the two-stage roast of arsenopyrite bearing materials (Rumiantsev et al., 2016; Grund et al., 2005). In their first non-oxidizing stage i.e. mildly reducing conditions, they are roasted at lower temperatures of 400–450 °C in an oxygen deficient environment. This produces the volatile trivalent arsenic oxide (As_2O_3) and/or arsenic sulfide (As_2S_3) and avoids the formation of the harmful ferric arsenate $FeAsO_4$, which inhibits precious metal solubilisation by blocking the pores of the calcine (Valenzuela, 2000; Prasad et al., 1991). Hence, the roasting pretreatment should not only provide maximum base metals recovery, but also produce a calcine with porous structure which facilitates reagent diffusion through the reacting product layer improving the leaching kinetics of PGMs.

On referring to Fig. 3, if O_2 and SO_2 partial pressures are maintained at the values corresponding to the shaded region (right upper corner), the roasting process will yield $NiSO_4$ and $CuSO_4$. However, a limited portion of Cr and Fe conversion is unavoidable. It should be observed that the shaded region has a low oxygen partial pressure of around 10^{-13} to 10^{-12} bars, as compared to the oxygen partial pressure in air which is 0.213 bar (Rhoades and Bell, 2012). This is corroborated by the good leaching recoveries of copper and nickel from static air roasting systems (e.g. unvented electric muffle furnace) as reported in open literature (Zhao et al., 2015; Ferron et al., 2006; Baglin et al., 1985; Fursman, 1962).

2.2.2.2. Sulfation roast processes using sulfate compounds—Sulfation mechanisms. The typical temperature range of conventional sulfation roast is between 650 and 700 °C (Güntner and Hammerschmidt, 2012). The average retention time of solids in the roaster is highly dependent upon the feed materials' mineralogy. Generally longer roasting times convert more sulfide mineral to sulfate, but long roasting times may also decrease the economy of the process.

According to Norrgran (1985) the preferred time is from two to six hours. The sulfation process has also been referred to as acid baking, in particular when applied at temperatures up to 400 °C (Dimitrijevic et al., 2016). It must be emphasized that acid baking suffers from large amounts of iron that enter the solution as indicated by Eq. (2), requiring additional operation before copper recovery (Prasad and Pandey, 1998; Norrgran, 1985). Iron elimination remains a major operational problem in hydrometallurgy. Furthermore, chromium (III) is generated from the digestion of chromite ores with concentrated sulfuric acid as described in Eq. (3) (Ustaoglu and Geveci, 2007; Stauter and Um, 1977).



Harris et al. (2007) stated that the presence of even relatively small concentration of ferric iron causes problems to all conventional reagents used in solvent extraction of copper. On the other hand, Chou (1986) has investigated the production of nickel powder using hydrogen reduction, he suggested that iron, copper and cobalt concentrations in the nickel sulfate solution should not exceed 100 ppm each. Contaminants such as cadmium, boron, lead, chromium and calcium should not exceed a total of about 400 ppm. Therefore, the solubilisation of such impurities must be limited.

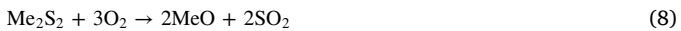
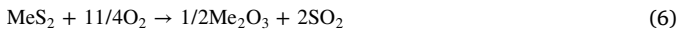
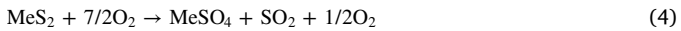
In general, the oxygen partial pressure and the temperature in the roaster are the two important parameters controlling the final products (La Brooy et al., 1994). High SO_2 contents are also favourable for the reaction. However, its level depends on the sulfur content of the feed material (Güntner and Hammerschmidt, 2012). According to Rambiyana et al. (2014) the pSO_2 should be kept high at more than 1%v/v to favour the formation of sulfates during the roasting of base metal sulfides. On the other hand, the roasting temperature is generally dictated by the decomposition temperatures of metal sulfates to be extracted (Hanf and Schmidt, 1979).

When a number of metals are to be extracted, as is usually the case, Norrgran (1985) stated that the temperature will approach the lowest decomposition temperature of the metal sulfates in question. According to Habashi (1969), sulfation roast of chalcopyrite at about 650 °C converts copper in water-soluble form and iron to Fe_2O_3 . Yu et al. (2014a) found that nickel ferrite ($NiFe_2O_4$), which is resistant to sulfation, forms at temperatures of more than 700 °C.

Norrgran (1985) suggested that the energetic decomposition temperatures of $FeSO_4$, $ZnSO_4$, $CuSO_4$, $CoSO_4$ and $NiSO_4$ are 480, 600, 670, 735 and 764 °C, respectively. Chromium is in its Cr(III) oxidation state in the chromite $FeCr_2O_4$ (Hawley et al., 2004). Udupa (1982) found that chromium (III) sulfate hexahydrate, $Cr_2(SO_4)_3 \cdot 6H_2O$, decomposes in two stages: The first begins at 100 °C and is complete at 400 °C; whereas the anhydrous $Cr_2(SO_4)_3$ decomposes in a single step in the 550–750 °C temperature range by forming Cr_2O_3 in the final residue.

Hence temperatures greater than the decomposition temperatures of iron and chromium sulfates, approximately 500 and 550 °C respectively, are required to promote the conversion of significant proportions of iron and chromium sulfates into their respective insoluble oxides. Note that sperrylite ($PtAs_2$)—the dominant Pt-containing mineral in the PGM-enriched chromitites under investigation (Lewins, 2006)—sublimes under 1 atm pressure at 1475 °C and its eutectic point (lowest

possible melting temperature) is 597 °C (Okamoto, 1990). Conventional sulfation roast can be schematized by one direct reaction step (Eq. (4)) or by three sequential reaction steps (Eqs. (5)–(12)) as described by Güntner and Hammerschmidt (2012).



According to the three sequential steps mechanism, metal sulfides are first oxidized to metal oxides (Eqs. (5)–(8)), and then sulfur dioxide is oxidized to sulfur trioxide (Eq. (9)). The production of sulfur trioxide (SO_3) gas is critical in the formation of sulfates (Wilkomirsky, 2014). Its reaction in Eq. (9) is catalysed by metal oxides, such as Fe_2O_3 (Hanf and Schmidt, 1979).



Another way to increase $\text{SO}_{3(\text{g})}$ partial pressure in the roaster is through the introduction of sulfuric acid that decomposes at high temperatures to generate $\text{SO}_{3(\text{g})}$ according to the reaction in Eq. (10) (Safarzadeh et al., 2014). These authors found that the maximum amount of $\text{SO}_{3(\text{g})}$ was in the 450–500 °C temperature range, after which $\text{SO}_{3(\text{g})}$ started to decompose into $\text{SO}_{2(\text{g})}$ and $\text{O}_{2(\text{g})}$. The temperature dependence of the equilibrium constant for the dissociation reaction is described in Eq. (11), where K_c is the equilibrium constant and T (K) the temperature inside the reactor (Shin et al., 2009).

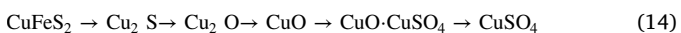


$$K_c = 1554.1 - 7.512T + 1.105 \times 10^{-2}T^2 - 2.450 \times 10^{-7}T^3 - 1.178 \times 10^{-8}T^4 + 7.182 \times 10^{-12}T^5 \quad (11)$$

Finally, metal oxides react with sulfur trioxide to form sulfates and/or basic sulfates (Eqs. (12) and (13)), wherein Me denotes mainly Cu, Ni, Co, Cr and Fe but also Ca and Mg. Güntner and Hammerschmidt (2012) stated that high water content at slurry feeding is supposed to promote the formation of copper sulfates. Although the precise mechanism is not yet understood, similar conclusions were reached by Guo et al. (2009) who indicated that the addition of water was necessary for good mixing and helped sulfation reactions.

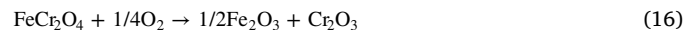
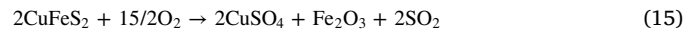


Prasad and Pandey (1999) have carried out studies on chalcopyrite oxidation in static air bed conditions, they observed that its sulfation roast route with ferric oxide proceed through the formation of copper sulfate from copper sulfide ($\text{Cu}_2\text{S}/\text{CuS}$) generated from chalcopyrite (Eq. (14)), rather than direct conversion of chalcopyrite to copper sulfate. As such, the current authors believe that the sulfation roast under investigation may proceed within the 400–550 °C temperature range without oxygen overpressure (see Fig. 3).

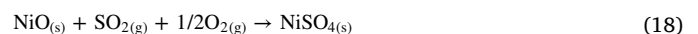
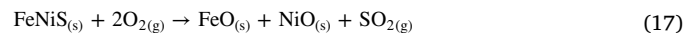


The main minerals in the ore under investigation are pentlandite ($\text{Ni}_3\text{Fe}_9\text{S}_8$), chalcopyrite CuFeS_2 , chromite FeCr_2O_4 and siliceous gangue materials. Thereby prominent species that the roasted calcine may contain at conventional temperatures are nickel oxide (NiO), nickel ferrite (NiFe_2O_4), heazlewoodite (Ni_3S_2), iron nickel monosulfide solid solutions ($(\text{Fe,Ni})_{1-x}\text{S}$), nickel sulfide (NiS), cupric oxide (CuO), bornite (Cu_5FeS_4), chalcocite (Cu_{2-x}S), copper ferrite (CuFe_2O_4), copper chromite (CuCr_2O_4), chromium oxide (Cr_2O_3), chromium (III) sulfide (Cr_2S_3), hematite (Fe_2O_3), magnetite (Fe_3O_4), as well as the water-soluble sulfates (Yu et al., 2012; Geng et al., 2012; Qi et al., 2011;

Hargreaves et al., 2006; Dumeignil et al., 2003; Prasad and Pandey, 1998; Jacob et al., 1992). The simplified decomposition reactions of chalcopyrite and chromite can be described as in Eqs. (15) and (16), respectively.



Yu et al. (2014b) observed that the sulfation of nickel sulfide was an extremely slow process, due to a dense nickel sulfate layer that inhibits further sulfation. According to Sohn and Wadsworth (2013) the sulfation of nickel in pentlandite proceeds through an oxidation roasting step to form NiO and SO_2 . In the second step, NiO reacts with SO_2 from the first step and O_2 to form NiSO_4 . These authors emphasized that the sulfation of pure NiO is very slow, because NiSO_4 is impermeable to SO_2 , since it forms a protective layer around unreacted NiO. The simplified basic reactions are summarised in Eqs. (17) and (18) (Fursman, 1962). However, NiSO_4 can be made permeable to gases by the addition of Na_2SO_4 which creates new sites for sulfates formation (Prasad and Pandey, 1998; Norrgran, 1985).



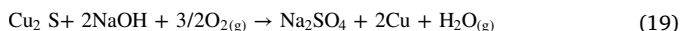
Lastly referring to sulfation roast, a loss in weight generally reveals the formation of oxides or the decomposition of metal sulfates, whereas a gain suggests the formation of sulfates (Basturkcu and Acarkan, 2016; Prasad and Pandey, 1998).

2.2.2.3. Sulfuric acid consumption. Primary nickel is produced from either nickel-iron-copper sulfide ores or nickeliferous lateritic ores typically assaying 1–3% Ni (Table 1) (Mihaylov, 2003). In high pressure acid leaching technology (HPAL), acid consumption is generally dictated by the magnesium and aluminium content of the ore. Mayze (1999) stated that the low magnesium content of Cawse required only 375 kg of acid per tonne of ore to maximize nickel recovery. Bulong, with a high magnesium content, is a relatively high acid consumer requiring 518 kg/t, while Murrin is moderate at 400 kg/t. This information is useful for safeguarding H_2SO_4 consumption in this project and future commercial application, albeit that sulfation roast and HPAL operate differently to extract nickel.

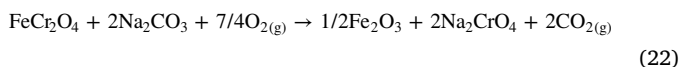
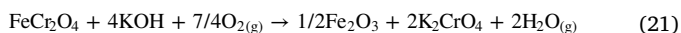
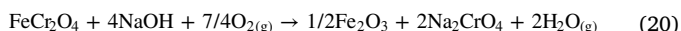
2.2.2.4. Selective sulfation roast process using alkali compounds. Alkali metal sulfates are also reported to promote the sulfation of nickel and copper concentrates in fluidised bed roasting (Prasad and Pandey, 1998; Norrgran, 1985). The process can be carried out by a number of sulfate promoters such as KOH, NaOH, K_2SO_4 , Na_2SO_4 , and Na_2CO_3 (Yu et al., 2014a,b; Guo et al., 2012, 2009; Frankiewicz, 1978). Baimbetov et al. (2015) stated that technologies of smelting sulfidic materials in molten alkali are environmentally friendly, due to zero release of sulfur containing gases. The reaction chemistry of copper sulfide bearing ores during alkali roasting using NaOH in the presence of atmospheric oxygen is described in Eq. (19).

Table 1
Head grade of some nickel producing industries (Köse, 2010).

Location Element (%)	Cawse	Moa Bay	Murrin Murrin	Bulong	New Caledonia
Ni	1	1.3	1.2	1.1	2.5
Co	0.07	0.12	0.08	0.08	0.04
Fe	18	48	22	21	12
SiO_2	42	9	42	43	47
Mg	1.6	0.55	3.7	4.6	15
Al	1.7	4.8	2.7	2.8	1.3
Mn	0.17	0.8	0.4	0.36	0.6
Cr	0.92	2	1	0.6	1.4



It must, however, be borne in mind that the alkali roasting process is also used worldwide for the extraction of sodium chromate from chromite ores (Qi et al., 2011; Tathavakar et al., 2005). Using NaOH and KOH in the 400–1000 °C temperature range and in oxidising atmosphere, Parirenyatwa et al. (2016) have revealed the formation of water-soluble Na₂CrO₄ and K₂CrO₄ as end products from chromite roasting (Equations (20) and (21)).



Likewise Antony et al. (2001) roasted FeCr₂O₄ and Na₂CO₃ at temperatures ranging between 900 and 1200 °C in oxidative atmosphere to form Na₂CrO₄ (Eq. (22)). Nayar et al. (2013) found that sodium chromate may be heated to 1000 °C without decomposition. This evidences its high thermal stability. Due to environmental concerns related to the safe disposal of Cr⁶⁺, it is an unlikely scenario that such a process would ever be utilized for the high chromite-bearing source under investigation.

3. Materials and methods

3.1. Materials—Run-of-mine ore

Table 2 displays the head grade and mineralogical composition of the supplied feed material obtained through Tescan Integrated Mineral Analysis (TIMA GM Model), XRF and fire assay analyses. Its mineralogical composition—serving as a guide—is essentially chromite (78.12%) with a small amount of sperrylite representing 0.02% (majority of the total platinum present). Although not detected by Tescan, previous analyses would suggest that palladium antimonide was the main palladium phase (Lewins, 2006).

Table 2

Chemical and mineralogical analyses of the high chromite content ore used in the sulfation-roast-leach tests.

Chemical analysis		Mineralogical analysis	Content (%)
Elements	Content (%)	Major phases	
Fe	13.60	Chromite (FeCr ₂ O ₄)	78.12
Cr	10.40	Chlorite – Clinocllore [(Mg,Fe,Li) ₆ AlSi ₃ O ₁₀ (OH) ₈] – [(Mg,Fe ²⁺) ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈]	11.16
Mg	7.18	Minor phases	
Al	5.35	Olivine (Mg ²⁺ ,Fe ²⁺) ₂ SiO ₄	3.23
Ca	0.42	Ferrotschermakite Ca ₂ [(Fe ²⁺ ,Mg) ₃ Al ₂] (Si ₆ Al ₂)O ₂₂ (OH) ₂	1.95
Ti	0.3190	Pentlandite (Fe,Ni) ₉ S ₈	1.51
Na	0.0310	Ankerite [Ca(Fe,Mg,Mn)(CO ₃) ₂	0.91
Ni	0.31	Rammelsbergite (NiAs ₂)	0.80
Mn	0.23	Chalcocopyrite (CuFeS ₂)	0.65
Zn	0.12	Magnesiogedrite [(Mg,Fe ²⁺) ₅ Al ₂ Si ₆ Al ₂ O ₂₂ (OH) ₂]	0.62
Cu	0.0646	Hematite/Magnetite [Fe ₂ O ₃ /Fe ₃ O ₄]	0.25
Si	2.64	Columbite [(Fe,Mn)Nb ₂ O ₆]	0.23
S	0.78	Traces phases	
C	0.11	Bornite (Cu ₅ FeS ₄)	0.10
V	0.0609	Covellite (CuS)	0.02
Co	0.0314	Sperrylite (PtAs ₂)	0.02
As	0.0185	Chromferide [Fe ₃ Cr _{1-x} (x = 0,6)]	0.02
Content (g/t)			
Pd	15.20		
Pt	12.80		
P	51.4		

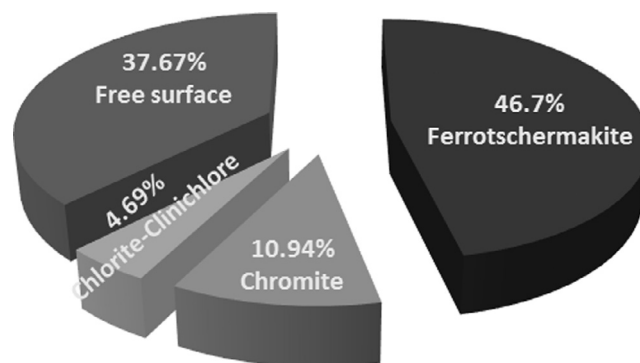


Fig. 4. Minerals locking sperrylite in the ore.

Copper (0.0646%) was contained in the minerals cuprite (Cu₂O), lautite (CuAsS) and bornite (Cu₅FeS₄). Pentlandite was detected to be around 1.51%. Nickel occurs also as arsenide (0.80%) in rammelsbergite (NiAs₂). The main nickel-bearing silicate minerals are chlorite-clinocllore (11.16%) and olivine (3.23%). These host minerals may contain an appreciable amount of nickel trapped inside, that may or may not be released during the pre-processing stages.

The minerals locking sperrylite in the ore are depicted in Fig. 4. Around thirty-eight percent occurred with an exposed face of PtAs₂ and the remainder as composite particles of chromite and various silicate minerals. Hence without a pre-processing stage, the accessibility of lixiviant to non-liberated PGM species would be expected to cause poor direct leachability.

Jones (2005) and Vermaak (1995) noticed that the chromite-rich UG-2 concentrate, with an average grain size of about 15 μm, required fine milling to about 80% of less than 75 μm in order to liberate PGM minerals. On the other hand, the Merensky concentrate which is amenable to the traditional sulfide matte smelting process was milled to around 55% of less than 75 μm (average grain size of circa 45 μm). The average grain size of the PGM minerals in the ore under investigation was found to be around 9 μm. With regard to the leaching process, Lottering et al. (2008) have made a distinction between liberation and surface exposure. They suggested that the measurement of area exposure is a very good indicator of the leachability, because only intrinsic inertness to leaching reagents can cause an exposed mineral to remain unleached. This is crucial as far as leaching is the key step in the process under investigation.

The feed material for the batch leaching test programme had been collected in relatively coarse grind size ranging from 710 μm to 2.8 mm. It was subjected to additional particle size reduction (P₈₀ < 75 μm) using a laboratory-size ring mill and afterward was kept in sealed fresh plastic bag containers—isolated from air effect—and stored in a freezer until used. Particle size distribution (PSD) by wet screening (Fig. 5) using Malvern Mastersizer 2000 was carried out at the CSIRO Process Science and Engineering branch, Waterford in Perth, Western Australia. The P₈₀ mean size of the particle fed to the sulfation roast process was around 64 μm.

3.1.1. Analytical instruments

The head grade and mineralogical composition of the supplied feed material were obtained through fire assay, XRF and Tescan Integrated Mineral Analysis (TIMA GM Model) operated by the John de Laeter Centre at Curtin University. Its mineralogical features after sulfation roast and that of the leach residue (water-insoluble fraction) were examined by the same means. The chemical composition of the leachate was analysed using ICP-MS.

Note that low-grade materials have generally heterogeneous or “spotty” distributions of valuable metals. This often presents difficulties in sampling and assay repeatability. Accordingly, leach residues were analysed with TIMA and fire assay to determine their residual metals

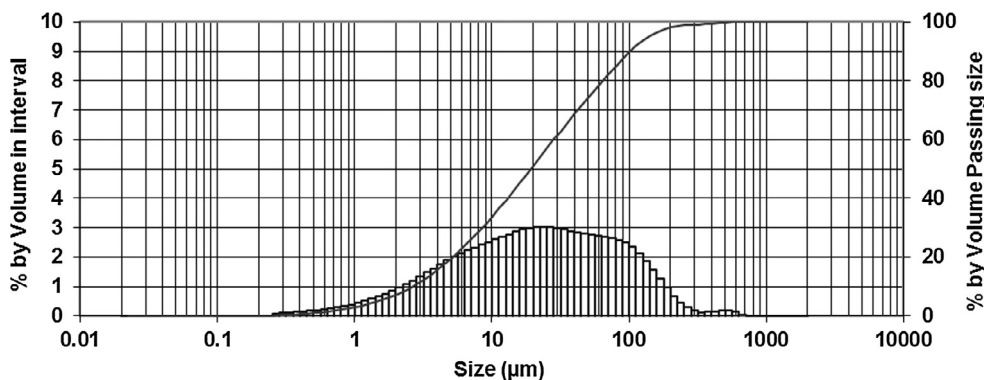


Fig. 5. Particle size distribution of the chromite-rich ore after ring-mill micronization.

content. Thereby the leached metal percentages were estimated from these fire assay and TIMA results and/or back-calculated from solution assay results.

3.2. Methods

3.2.1. Methodology—Experimental design

A factorial design was employed to optimize the process. Two sets of laboratory scale experiments were conducted using ore whose chemical and mineralogical compositions are displayed in Table 2. The first set consisted of sulfation roast tests designed to generate optimal operating conditions of the process. The second set of tests consisted of leaching studies using distilled water as leachant. The statistical approach was applied to combine these two experimental designs. The individual levels for the seven input factors are shown in Table 3. These independent variables were selected from the literature dedicated to the sulfation roast-leach processes of copper and/or nickel ores (concentrates).

The design of experiments chosen for this study was the 2^{7-3} fractional factorial design for the seven independent variables. The design matrix produced twenty-four treatment combinations including eight replicates at the centre point, to evaluate the preliminary significance of these variables, the experimental error and the reproducibility of the data as well as the curvature. The experimental design layout and results are listed in Table 4. At each combination of the process settings, the leaching percentages were recorded.

The goal was to maximize copper and nickel leaching rate while trying to find conditions that would minimize both reagent consumption and co-leaching of PGMs and other species. Replicate experiments were also conducted in order to quantify the reproducibility of the sulfation roast-leach tests. Experiments were performed in randomized order to minimize the effects of extraneous or nuisance variables. Experimental design and statistical treatment of the results were performed using Design-Expert® version 9.0.6.

Table 3

Independent variables and their respective levels used in the factorial design of sulfation-roast-leach tests.

Operating factors	Notation	Levels		
		−1	0	+1
H ₂ SO ₄ addition (wt%), (kg H ₂ SO ₄ /t ore)	A	30, (462)	40, (856)	50, (1250)
Na ₂ SO ₄ addition (wt%), (kg Na ₂ SO ₄ /t ore)	B	5, (76.92)	7.5, (163.45)	10, (250)
Roasting temperature (°C)	C	400	475	550
Roasting time (min)	D	120	150	180
Leaching temperature (°C)	E	25	52.5	80
Leaching duration (min)	F	180	810	1440
Oxygen addition (mL/min)	G	0	250	500

3.2.2. Sulfation roast procedure

The sulfation roast experiments were carried out at a laboratory scale by mixing, on weight percent basis, known amount of raw ore (P₈₀ of < 75 µm, 0.78% sulfide content) with concentrated H₂SO₄ (98% purity, ρ = 1.84 g/cm³) and Na₂SO₄ (99% purity) in a porcelain crucible. Unless otherwise indicated, the sticky paste-like material was relatively evenly distributed through the crucible wall and had an approximate depth (thickness) of less than 3 mm, eliminating local overheating (formation of ferrites) and ensuring uniform oxidation throughout the bed. The charged and covered crucible was placed in an unvented electric or static air roast muffle furnace equipped with a programmable temperature controller, and was gradually heated under normal atmospheric pressure and oxygen partial pressure conditions at a linear heating rate ranging from 6 to 10 °C/min.

The roasted sample was allowed to cool to room temperature inside the furnace. In order to break up formed particle aggregates, the calcine was reground to 100% passing through a size 75 µm screen, and weighed before leaching with distilled water. It is of interest to note the observation made by Tshiongo et al. (2010) that calcine cooling rate affects the leaching of base metals as it changes the phase distribution in the calcine and base metals distribution within the phases. A fast cooling prevented the crystallization that results in the formation of amorphous and glassy phased calcine, encapsulating metal values and lowering their solubility.

3.2.3. Leaching procedure

Except where mentioned, leaching experiments were carried out using 500 mL of distilled water. Once the desired temperature was reached, the calcine from the previous step (10 g, solid density of 2% w/v, i.e. at a solid-to-liquid ratio of 1:50) was added into the reactor, from which point onwards the reaction time was measured. It is pertinent to mention that the dissolved oxygen content in aqueous solutions can be increased by the process of aeration.

The efficiency of oxygen transfer depends on many factors, including bubble size and flow rate (Navisa et al., 2014; Karimi et al., 2013). To ascertain its relative importance on the leaching performance of sulfates (if involved then sulfation roast no successful), oxygen was continuously fed into the slurry at 500 mL/min through a microporous sparger located 1 cm above the impeller in order to increase the residence time of each bubble in the solution to allow a better oxygen transfer rate. Sulfates have fast leaching rates, due to their direct dissolution into the leachant (water) without chemical transformation involved (Yu et al., 2012).

Agitation was provided by an overhead sealed-shaft stirrer driven at a constant speed of 600 rpm, to ensure full suspension of solids and to minimize external mass transfer resistance. The leaching time was extended to 48 h, in order to assess its effect on the reaction mixture and to establish equilibrium conditions. To prevent further reaction with the leached material which may have been carried over from the process, aliquots of 3 mL were collected at specific timed intervals through

Table 4
Experimental design layout and results.

Run	Seven independent variables							SIX responses (%)					
	H ₂ SO ₄ addition (wt %)	Na ₂ SO ₄ addition (wt %)	Roasting temperature (C°)	Roasting time (min)	Leaching temperature (C°)	Leaching time (min)	Oxygen addition (mL/min)	Cu	Ni	Pt	Pd	Fe	Cr
1	+1	+1	+1	+1	+1	+1	+1	47.34	99.07	0.11	0.43	9.55	23.18
2	+1	+1	+1	-1	+1	-1	-1	59.17	94.70	0.23	4.99	14.51	25.46
3	+1	+1	-1	+1	-1	-1	-1	44.59	52.70	0.57	11.56	18.83	11.54
4	-1	-1	+1	+1	+1	-1	-1	55.33	60.77	*	0.31	3.59	1.20
5	-1	-1	-1	+1	-1	+1	+1	62.23	59.17	*	*	6.40	2.28
6	-1	+1	+1	-1	-1	-1	+1	34.62	55.70	*	0.85	2.25	1.81
7	0	0	0	0	0	0	0	51.45	75.40	*	*	5.73	6.29
8	0	0	0	0	0	0	0	56.39	83.91	*	*	5.99	6.46
9	-1	+1	-1	+1	+1	-1	+1	62.79	64.13	*	*	3.37	1.89
10	0	0	0	0	0	0	0	63.69	77.81	*	*	6.39	6.12
11	0	0	0	0	0	0	0	75.94	83.24	*	*	7.56	6.33
12	0	0	0	0	0	0	0	51.57	83.44	*	*	6.05	6.43
13	-1	+1	+1	+1	-1	+1	-1	34.68	58.06	*	*	3.83	2.04
14	+1	-1	-1	-1	+1	-1	+1	76.59	96.24	0.10	2.71	11.04	17.39
15	+1	+1	-1	-1	-1	+1	+1	62.67	82.30	0.34	8.10	27.31	19.50
16	+1	-1	+1	+1	-1	-1	+1	60.49	45.33	0.10	7.52	6.59	2.81
17	0	0	0	0	0	0	0	51.69	80	*	*	6.37	6.74
18	+1	-1	-1	+1	+1	+1	-1	78.07	94.78	*	*	11.93	18.51
19	-1	-1	-1	-1	-1	-1	-1	58.38	53.77	*	*	7.43	1.83
20	0	0	0	0	0	0	0	61.15	80.70	*	*	6.48	6.07
21	0	0	0	0	0	0	0	68.54	74.13	*	*	6.64	5.78
22	-1	+1	-1	-1	+1	+1	-1	71.67	78.23	*	*	4.52	2.26
23	+1	-1	+1	-1	-1	+1	-1	68.49	66.81	*	4.64	11.94	9.37
24	-1	-1	+1	-1	+1	+1	+1	70.81	84	*	*	2.62	1.32

(*) denotes below detection limit 0.1 µg/L for Pd and 0.05 µg/L for Pt, while (-1), (+1) and (0) are low, high and centre point levels of the independent variables.

0.45 µm pore size syringe filters, and analysed for dissolved metals by ICP-MS. The leach residue was washed thoroughly several times with distilled water to remove any physically attached ions or any unreacted ligands (reagents), and then filtered under vacuum using Whatman N° 1 paper, oven-dried at 50 °C for 72 h, and kept until required.

3.2.4. Leaching reactor

The batch vessel used in this work was a 1500 mL (working volume) double jacketed glass reactor provided with a tapering conical bottom—100 mm interior diameter, 243 mm in height—fitted with four symmetrically fixed baffles and water inlet/outlet connected to a temperature-controlled water bath. The conical configuration facilitates good mixing. The flow pattern gives adequate solid suspension. Singh et al. (2011) argued that reactors with conical bottoms have satisfactory flow patterns, owing to very low off bottom clearance of the impeller.

The vessel had openings in the lid to introduce a dispersion tube for oxygen and a pH electrode, to withdraw solution samples, and a central opening to fix an anchor propeller stirrer for mixing the solution. The reactor was also equipped with a mercury thermometer and a cooling reflux condenser connected to a chilled water line that allows continuous return of volatile materials to the reaction mixture, reducing evaporation losses of essential ingredients as oxygen (99% purity) was bubbled throughout the tests. To maintain the water balance, evaporation losses were compensated by adding distilled water before sampling. All open ports on the lid were plugged with rubber stoppers to seal the reactor.

4. Results and discussion

The use of resolution (IV) design prevents main factors from being aliased with any other main effects as well as two-factor interactions. Contrariwise main effects are aliased with third- and higher order interactions. However, second-order interactions are aliased with each other (Zolgharnein and Shahmoradi, 2010). Thereby, current fractional factorial design allows independent estimation of individual main effect, as it is often true that high-order interactions (triple or above)

tend to become negligible (Tinoco et al., 2011). The ranking of the importance of each factor and/or interaction in the overall process depends on the numerical value of the coefficient of each factor or its interaction in absolute value (Passos et al., 2006).

4.1. Screening important factors

Main factor analysis (Table 5) shows the effect of each individual factor on the measured responses. It should be noted that H₂SO₄ addition was the most influential factor among all others. Nickel dissolution apparently outpaced that of copper at a comparatively low H₂SO₄ concentration (≈ 462 kg/t ore), which is probably due to the easier decomposition of the nickel phases; pentlandite and rammeisbergite (Table 4).

The decrease of copper extraction with the increase of roasting temperature is not consistent with the higher decomposition temperature of copper sulfates which is in the range of 650–700 °C. The decline may be attributed to the partial decomposition of corresponding copper sulfates at higher temperatures (Guo et al., 2009).

The eutectic in the NiSO₄-Na₂SO₄ system is at approximately 670 °C (Yu et al., 2014b), which is above current roasting temperatures. This may explain the non-involvement of Na₂SO₄ in nickel sulfation. Basturkcu and Acarkan (2016) stated that the catalytic activity of Na₂SO₄ depends on its dosage and reaction temperature. In this context, nickel extraction without Na₂SO₄ addition was found to be 87.1% (not shown graphically) with a decrease in H₂SO₄ addition from 462 to 428.57 kg/t ore in order to preserve the weight percent calculations.

The leaching temperature and duration had a positive effect on nickel extraction. It should be noted that increasing the temperature makes any passivation layer less stable (Bahamòndez et al., 2016). However, excessive extraction time might not be effective for the extraction process because, from an industrial point of view, longer extraction time means lower efficiency of equipment utilization. Oxygen bubbling at the leach stage was the only factor not involved in any response. This is consistent with the leaching of sulfate compounds.

Table 5
Estimate of main effects of process variables on the different responses.

Term	Cu			Ni			Pt			Pd			Fe			Cr		
	Adjusted coeff.	% contr.	p value	Adjusted coeff.	% contr.	p value	Adjusted coeff.	% contr.	p value	Adjusted coeff.	% contr.	p value	Adjusted coeff.	% contr.	p value	Adjusted coeff.	% contr.	p value
H ₂ SO ₄ addition	-7.05	-	-	7.38	16.28	0.0001	0.091	30.01	0.002	2.42	39.16	0.0001	0.26	68.34	0.0001	1.21	73.65	0.0001
Na ₂ SO ₄ addition	-	26.67	0.0018	-	-	-	0.066	15.74	0.015	-	-	-	-	-	0.30	0.30	4.61	0.0309
Roasting temp.	-5.38	15.51	0.0124	-	-	-	-	-	-	-	-	-	-0.11	12.37	0.0016	-	-	-
Roasting time	5.98	19.14	0.0063	-4.86	7.05	0.005	-	-	-	-	-	-	-	-	-	-	-	-
Leaching temp.	-	-	-	12.38	45.79	0.001	-	-	-	-1.51	15.28	0.0051	-	-	-	0.33	5.36	0.0212
Leaching time	-	-	-	6.19	11.46	0.0008	-	-	-	-	-	-	-	-	-	-	-	-
Oxygen addition	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Centre point	-0.443	0.035	0.8970	8.22	6.73	0.0063	-0.091	10.0	0.046	-2.57	14.66	0.0059	-0.047	0.78	0.3696	-0.12	0.26	0.5880

(-) denotes factor not in the model.

An advantage of the sulfation roast-leach process is that the pH of the final leach solution was approximately 2, which is beneficial for downstream recovery processing of base metals. Such possibility of acid regeneration accomplished through water reacting with residual SO₃ implies low acid consumption. This significantly reduces neutralization costs as currently practiced in HPAL. Lastly, because the interest regions of factors are different, several variables need to be controlled, i.e., reagent concentrations, roasting temperature, etc., there is consequently a need for a practical optimization of the roast-leach process.

4.2. Multiple response optimization technique

4.2.1. Desirability function approach—Setting optimization criteria

The desirability function is a popular and established technique for simultaneous determination of optimum settings of input variables that can determine optimum performance levels for one or more responses (Azharul et al., 2009). Desirability is an objective function that ranges from zero outside the limits, to one at the goal. The approach is based on the idea that, when one of the quality characteristics of an industrial process or product with many characteristics is not in the desired limits, then the entire quality of the industrial process or the product is not desirable (Pasandideh and Niaki, 2006).

The desired goal was selected by adjusting the weight or importance that might alter its characteristics. Importance ranges from 1 to 5. It is a tool for changing relative priorities to achieve established goals for some or all variables. The individual desirability functions *d_i* – generated based upon the type of each characteristic – are calculated as shown in Eq. (23).

$$d_i = \begin{cases} 0 & y_i < L \\ \left(\frac{y_i - L}{T - L}\right)^w & L \leq y_i \leq T \\ 1 & y_i > T \end{cases} \tag{23}$$

where *L*, *T* stand for lower limit of the response (*y_i*) and its target value, respectively.

The main effects of each factor upon responses were ascertained through ANOVA. The results shown in Table 5 indicate that H₂SO₄ concentration was the most significant process factor, due to its high percentage contribution among other process parameters.

A weight (*w*) can be assigned to each goal to adjust the shape of its particular desirability function. Weight gives added emphasis to upper and lower bounds or emphasizes target values. The maximum weight is 10. Selecting *w* > 1 places more emphasis on being close to the target value, and selecting 0 < *w* < 1 makes this less important. The individual desirabilities are then combined using the geometric mean, which gives the overall desirability *D* expressed in Eq. (24).

$$D = [d_1(y_1) \times d_2(y_2) \times \dots \times d_r(y_r)]^{\frac{1}{r}} \tag{24}$$

with (*r*) denoting the number of responses.

Design-Expert® software has inbuilt optimization tool. Table 6 shows the settings provided to the software package and the final result obtained in numerical optimization is tabulated in Table 7. There were 100 solutions found but solution with the highest desirability and/or yield was selected as final result.

The bar graph depicted in Fig. 6 shows how well each variable satisfied the criteria and the overall combined desirability. Values near one are recommended. A value of one represents the ideal case, while a zero indicates that one or more responses fall outside desirable limits.

4.2.2. Predicted optimal conditions

Under the optimized conditions as suggested by the present study (81% overall desirability), 90.40% Ni and 69.45% Cu could theoretically be recovered through water-leach after 2 h of sulfation roast (Table 7). However, the actual test (Fig. 7) resulted in 89.86% Ni and 76.83% Cu extracted using 462 kg H₂SO₄/t ore.

The results in Fig. 7 shows that most of the leaching occurred in the

Table 6
Setting goal for each factor and response for formulation of optimized conditions.

Name	Goal	Lower limit	Upper limit	Importance
A: H ₂ SO ₄ addition	Minimize	30	50	3
B: Na ₂ SO ₄ addition	Minimize	0	10	3
C: Roasting temperature	In range	400	550	3
D: Roasting time	In range	120	180	3
E: Leaching temperature	In range	25	80	3
F: Leaching time	In range	180	1440	3
G: Oxygen addition	*	*	*	*
Cu extraction	Maximize	34.62	99	5
Ni extraction	Maximize	45.33	99.07	5
Pt extraction	Minimize	0	2	4
Pd extraction	Minimize	0	15	4
Fe extraction	Minimize	2.25	5	3
Cr extraction	Minimize	1.2	5	3

(*) indicates that factor is not in any model.

Table 7
Predicted optimum conditions for the seven process variables to produce maximum or minimum in the six responses.

Optimized process variables							Predicted responses					
A	B	C	D	E	F	G	Cu	Ni	Pt	Pd	Fe	Cr
30	5	550	120	80	1440	0	69.45	90.40	0	0	3.07	2.02

first 60 min (first data point) achieving 86% Ni extraction. Small increase (4%) was attained after 24 h and then the curve plateaued at around 90%. Such a prolonged leaching may be beneficial in increasing nickel extraction. However, the overall capacity of the plant and its operating costs may also increase following an extended process. Thereby optimal duration should be selected based on whether the extra nickel credit compensates the production expenses. Nevertheless for research purposes only, 24 h was selected as the effective leaching time to ensure complete equilibration.

4.3. Experimental error—Tests reproducibility

The accuracy of fit of the model was checked by correlation coefficient and/or coefficient of variation (coefficient of variability or

coefficient of variance). Note that the coefficient of variation (= 100 * standard deviation/mean) is a measure of the reproducibility of a model (Mohammed and Ahmad, 2010; Mpinga et al., 2014a). A model can be considered reasonably reproducible if its coefficient of variation is not greater than 10% (Chowdhury et al., 2012). It was observed in this study that the coefficient of variation varies from 3.83 to 9.71%. To establish the degree of reproducibility of the findings, four simulation tests were performed under optimum conditions in Table 7. The experimental error related to the reproducibility of the tests was evaluated at ± 8% i.e., the precision and accuracy of the method were satisfactory.

4.4. Empirical predictive ANOVA model

The fundamental objective of a factorial design is to develop a predictive model. All experiments were performed according to statistical designs, in order to develop predictive regression models used for optimization. Response surface methodology (RSM) makes it possible to represent independent process parameters in quantitative form as in Eq. (25).

$$Y = f(X_1, X_2, X_3, \dots, X_n) \pm \epsilon \tag{25}$$

where Y is the response, f is the response function, ε is the experimental error and X₁, X₂, X₃, X_n, are independent parameters. The true relationship between Y and X_n may be complicated and, in most cases, it is unknown. It is noteworthy that the response surface methodology does not elucidate the mechanism of the processes studied, but only ascertains the effects of factors upon responses. After discarding insignificant terms i.e. terms having a probability p-value > 0.05, the resultant models for describing base metal copper and nickel solubilisation, can be described in term of actual factors by Eqs. (26) and (27).

$$Cu_{\text{Extraction}} = +59.10 - 7.05B - 5.38 C + 5.98E \tag{26}$$

$$Ni_{\text{Extraction}} = +74.35 + 7.38A - 4.86 D + 12.38 E + 6.19F \tag{27}$$

Apart from correlation coefficients (R²), the closeness of fit to the experimental data can be tested either by normal probability plot of the residual between the response and the prediction or by comparing the experimental data against the data predicted by the models used for the regression analysis (Teng et al., 2012; Sheridan et al., 2002). With regard to copper extraction, the Predicted (Pred) R-Squared of 0.91 is in reasonable agreement with the Adjusted (Adj) R-Squared of 0.85 i.e. the

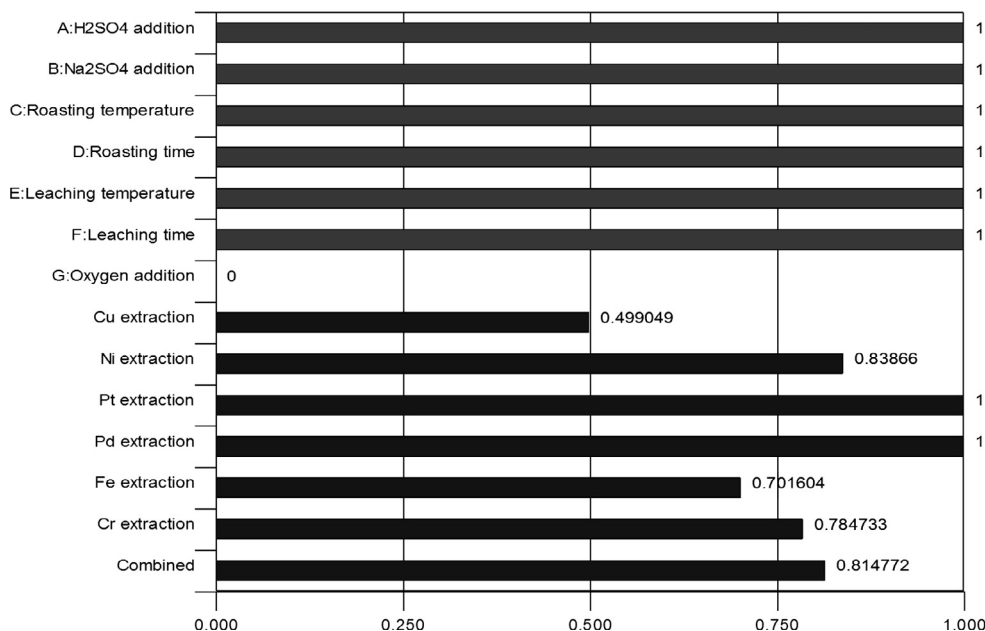


Fig. 6. Desirability bar graph for simultaneous optimization of multiple responses.

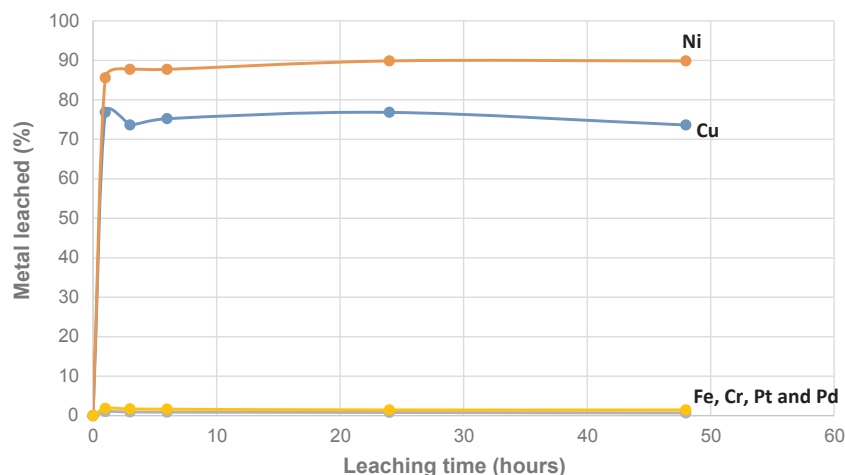


Fig. 7. Formation of water-soluble metal species as a function of leach duration (low-grade Cu-Ni-PGMs ore roasted at 550 °C for 2 h with 30 wt% H₂SO₄ (462 kg/t ore) and 5 wt% Na₂SO₄ addition (76.92 kg/t)). Leaching conditions: distilled water, pulp density of 2%w/v, without oxygen addition, rotational rate of 600 rpm at 80 °C.

difference is less than 0.2. Similarly for nickel extraction, the Pred R-Squared of 0.97 is also in reasonable agreement with the Adj R-Squared of 0.93; i.e. the difference is less than 0.2. Therefore, the models are significant for the solubilisation process of base metals.

4.5. Chemical and mineralogical characterization of calcine and leach residues

Chemical and mineralogical changes brought by the sulfation roast-water leach were identified by means of fire assay and TIMA. Mineralogical examination (Table 8) has indicated that more than one-half of the calcines consisted of chromite. This is apparent on a microscopic scale the fairly uniform chromite composition of the ore and does not vary significantly from one particle to another. The remainder was largely a mixture of chlorite – clinocllore and olivine. There was no pentlandite or chalcopyrite in the calcines.

Mineralogical studies have also indicated that unleached platinum in all leach residues was sperrylite. Note that the lowest melting temperature in the As-Pt system (eutectic) is approximately 597 °C (Okamoto, 1990), which is higher than Panton's roasting temperature of 550 °C (adopted in this work). Therefore, temperatures of more than the eutectic point are required to accelerate the thermal decomposition of sperrylite. However, no Pd mineral was detected (TIMA) in either sample, although the ore head sample contained 15.20 g/t and the residue was upgraded.

Table 8

Elemental analysis and mineralogical characterization of the ore before and after roast-leach based on TIMA and fire assay analyses.

Chemical analysis (%)	Raw ore	Calcine roaster	Water-leach residue
Ni	0.31	0.314	0.031
Cu	0.065	0.067	0.015
Fe	13.60	13.51	16.48
Cr	10.40	10.40	13.21
<i>Content (g/t)</i>			
Pt	12.80	12.83	15.24
Pd	15.20	15.20	17.14
<i>Mineral (%)</i>			
Chromite	78.12	96.30	96.36
Chalcopyrite (CuFeS ₂)	0.65	*	*
Pentlandite (Fe,Ni) ₉ S ₈	1.51	*	*
Rammelsbergite (NiAs ₂)	0.80	0.21	*
Sperrylite (PtAs ₂)	0.02	0.11	5.22

(*) indicates undetected.

5. Conclusions

A fractional factorial design investigating the levels of H₂SO₄ (sulfating agent), Na₂SO₄ (catalyst), roasting temperature, roasting time, leaching temperature, oxygen addition at the leaching stage and leaching duration on the dissolution efficiency of various metals including copper, nickel, iron, chromium and PGMs was conducted. The first and most important conclusion that can be made is that nickel and copper can effectively be leached from a complex, chromite-rich Cu-Ni-PGM ore using a sulfation roast-leach method. The results demonstrated that within the parameters of the experiments, the amount of H₂SO₄ addition was the most influential factor to control, whereas the effect of Na₂SO₄ addition on Ni was not statistically significant.

Oxygen bubbling at the leach stage was the only factor not involved in any response. This is consistent with the leaching of sulfate compounds. The theoretical optimum conditions found were 30 wt% (462 kg/t) H₂SO₄, 5 wt% (76.92 kg/t) Na₂SO₄, roasting temperature of 550 °C, roasting time of 120 min, leaching temperature of 80 °C and leaching time of 1440 min to achieve 69.45% copper and 90.40% nickel recovery. Actual test resulted in 89.86% Ni and 76.83% Cu extracted with 462 kg H₂SO₄ consumed /t ore. The extraction of nickel without Na₂SO₄ addition (not from the predictive modelling) was found to be 87.1% with a decrease in H₂SO₄ addition from 462 to 428.57 kg/t ore in order to preserve the weight percent calculations. The experimental error related to the reproducibility of the tests was evaluated at ± 8% i.e., the precision of the method was satisfactory.

It is foreseen that the use of low temperature leaching at atmospheric pressure will save considerable amount of energy thereby minimising operating costs. While unconcentrated ore was used in the roasting process, ideally the technique can use a rougher flotation product—a considerable amount of ore weight will be rejected—thus reducing separation costs and saving valuable minerals (e.g. sperrylite) that may be lost in making cleaner concentrates. Only a low percentage of chromium and iron (10.40 and 13.60% in the ore, respectively) accompanies copper and nickel as water-soluble sulfates (0.80 and 1.46%, respectively). Since chromite comprises about 78.12% of the ore, any decrease in its solubilisation is of significance to the overall process. High temperatures of more than 550 °C are required in order to break down bonds or at least modify the arsenide lattice to align downward platinum recovery process.

Acknowledgements

The authors are grateful for the financial support provided by the

Curtin International Postgraduate Research Scholarships (CIPRS) at Curtin University, in Perth, Western Australia. The permission of Panoramic Resources Plc. to publish this work is also gratefully acknowledged. The research was sponsored by Panoramic Resources Ltd and the Minerals Research Institute of Western Australia (MRIWA) and their financial support is kindly acknowledged. Panoramic Resources also provided the samples for the research.

References

- Antony, M.P., Tathavadkar, V.D., Calvert, C.C., Jha, A., 2001. The soda-ash roasting of chromite ore processing residue for the reclamation of chromium. *Metall. Mater. Trans. B* 32 (6), 987–995.
- Azharul, I.M., Sakkas, V., Triantafyllos, A.A., 2009. Application of statistical design of experiment with desirability functions for the removal of organophosphorus pesticide from aqueous solution by low-cost material. *J. Hazard. Mater.* 170 (1), 230–238.
- Baglin, E.G., Gomes, J.M., Carnahan, T.G., Snider, J.M., 1985. Recovery of platinum, palladium, and gold from Stillwater Complex flotation concentrate by a roasting-leaching procedure. In: *Complex Sulfides-Processing of Ores, Concentrates and by-Products*, San Diego, California, pp. 10–13.
- Bahamóndez, C., Castro, R., Vargas, T., Arancibia, E., 2016. In situ mining through leaching: experimental methodology for evaluating its implementation and economic considerations. *J. South Afr. Inst. Min. Metall.* 116 (7), 689–698.
- Baimbetov, B.S., Aitenov, K.D., Bekisheva, A.A., Abdikerim B.E., 2015. Metallic sulphide and sodium carbonate interacting processes. *Metall. Min. Ind.* (11).
- Basturkcu, H., Acarkan, N., 2016. Separation of nickel and iron from lateritic ore using a digestion–roasting–leaching–precipitation process. *Physicochem. Probl. Miner. Process.* 52 (2), 564–574.
- Bax, A., Dunn, G.M., Lewins, D., 2009. Recovery of Platinum Group Metals. USA Patent 7544231 B2.
- Breuer, P.L., Hewitt, D.M., Sutcliffe, C.A., Jeffrey, M.I., 2009. The quantification of cyanide and its reaction products during leaching and cyanide destruction processes. In: *World Gold 2009 Conference. The Southern African Institute of Mining and Metallurgy, Johannesburg*, pp. 287–294.
- Brierley, J.A., Brierley, C.L., 2001. Present and future commercial applications of biohydrometallurgy. *Hydrometallurgy* 59 (2), 233–239.
- Chou, E.C.J., 1986. Production of high surface area nickel powder. United States Patent 4758266.
- Chowdhury, Z.Z., Zain, S.M., Khan, R.A., Ahmad, A.A., Khalid, K., 2012. Application of response surface methodology (RSM) for optimizing production condition for removal of Pb(II) and Cu(II) onto Kenaf fiber based activated carbon. *Res. J. Appl. Sci. Eng. Technol.* 4 (5), 458–465.
- Dimitrijevic, M.D., Urosevic, D.M., Jankovic, Z.D., Milic, S.M., 2016. Recovery of copper from smelting slag by sulphation roasting and water leaching. *Physicochem. Probl. Miner. Process.* 52 (1).
- Dumeignil, F., Amano, H., Wang, D., Qian, E.W., Ishihara, A., Kabe, T., 2003. Study of the sulfidation process of $\text{CrO}_3\text{-Al}_2\text{O}_3$ hydrodesulfurization catalysts by a ^{35}S -labeled H_2S pulse tracer method. *Appl. Catal. A* 249 (2), 255–263.
- Ellis, S., 2003. Ultra Fine Grinding—A Practical Alternative to Oxidative Treatment of Refractory Gold Ores. Townsville: QLD, pp. 11–17.
- Ferron, C.J., Hamilton, C.C., Valeyev, O., McKay, N., 2006. The Effect of the Mineralogy of the Platinum Group Metals on their Leachability During the Platsol® Leach Process. SGS Minerals Services Technical Paper, 3.
- Frankiewicz, T.C., 1978. U.S. Patent No 4,110,106. U.S. Patent and Trademark Office, Washington, DC.
- Furman, O.C., 1962. Recovery of Mineral Values in Cupriferous and Nickeliferous Pyrrhotite. US Department of the Interior, Bureau of Mines.
- Geng, Q., Zhao, X., Gao, X., Yang, S., Liu, G., 2012. Low-temperature combustion synthesis of CuCr_2O_4 spinel powder for spectrally selective paints. *J. Sol-Gel. Sci. Technol.* 61 (1), 281–288.
- Green, B.R., Smit, D.M.C., Maumela, H., Coetzer, G., 2004. Leaching and recovery of platinum group metals from UG-2 concentrates. *J. S. Afr. Inst. Min. Metall.* 104 (6), 323–331.
- Grund, S.C., Hanusch, K., Wolf, H.U., 2005. Arsenic and Arsenic Compounds. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Güntner, J., Hammerschmidt, J., 2012. Sulphating roasting of copper-cobalt concentrates. *J. South Afr. Inst. Min. Metall.* 112 (6), 455–460.
- Guo, Q., Qu, J.K., Qi, T., Wei, G.Y., Han, B.B., 2012. Activation pretreatment of limonitic laterite ores by alkali-roasting using NaOH. *Int. J. Miner., Metall., Mater.* 19 (2), 100–105.
- Guo, X., Li, D., Park, K.H., Tian, Q., Wu, Z., 2009. Leaching behavior of metals from a limonitic nickel laterite using a sulfation–roasting–leaching process. *Hydrometallurgy* 99 (3), 144–150.
- Habashi, F., 1969. Principles of Extractive Metallurgy, vol. 1 CRC Press.
- Hanf, N.W., Schmidt, C.G., 1979. The roasting and leaching of Witwatersrand pyrite concentrates. *J. S. Afr. Inst. Min. Metall.* 79 (13), 365–371.
- Hargreaves, J.S., Jackson, S.D., Webb, G. (Eds.), 2006. Isotopes in heterogeneous catalysis, vol. 4 World Scientific.
- Harris, G.B., White, C.W., Liu, Z., 2007. Recovery of copper from oxide waste by leaching, ion exchange and electrowinning. Paper presented at Symposium on Copper Hydrometallurgy, Sixth International Copper-Cobre Conference Toronto, August 25–30.
- Hawley, E.L., Deeb, R.A., Kavanaugh, M.C., Jacobs, J.A., 2004. Treatment technologies for chromium (VI). Chromium (VI) handbook, pp. 275–309.
- Hunt, A., Kraus, G.A., 2013. Element Recovery and Sustainability (No 22). Royal Society of Chemistry.
- Jacob, K.T., Kale, G.M., Waseda, Y., 1992. Gibbs energy of formation of CuCrO_4 and phase relations in the system Cu-Cr-O below 735 K. *Thermochim. Acta* 208, 341–348.
- Jones, R.T., 2002. ConRoast: DC arc smelting of dead-roasted sulphide concentrates, Sulfide Smelting 2002. Stephens, R.L., Sohn, H.Y. (Eds.), TMS (The Minerals, Metals & Materials Society), Seattle, 17–21 February 2002.
- Jones, R.T., 2005. An overview of Southern African PGM smelting. Nickel and Cobalt 2005: Challenges in Extraction and Production, pp. 147–178.
- Karimi, A., Golbabaei, F., Mehrnia, M.R., Neghab, M., Mohammad, K., Nikpey, A., Pourmand, M.R., 2013. Oxygen mass transfer in a stirred tank bioreactor using different impeller configurations for environmental purposes. *Iranian J. Environ. Health Sci. Eng.* 10 (1), 1.
- Kellogg, H.H., 1964. Critical review of sulfation equilibria. *Trans. Metall. Soc. AIME* 230 (7), 1622.
- Köse, C.H., 2010. Hydrometallurgical Processing of Lateritic Nickel Ores. MSc Thesis Middle East Technical University, Ankara, Turkey.
- Kshumaneva, E.S., Kasikov, A.G., Gromov, P.B., 2014. Study of the sulfation of platinum-containing concentrate of Co-Ni thiospinels. *Russ. J. Appl. Chem.* 87 (2), 128–134.
- La Brooy, S.R., Linge, H.G., Walker, G.S., 1994. Review of gold extraction from ores. *Miner. Eng.* 7 (10), 1213–1241.
- Lawrence, R.W., López, O., 2011. Improving the economics of gold-copper ore projects using SART technology. Gold 2011, Montreal, Canada.
- Lewins, J., 2006. Platinum service. *Mater. World (January)* 30–32.
- Lewins, J., Greenaway, T., 2004. The Panton Platinum-Palladium Project. The Australian Institute of Mining and Metallurgy Bulletin, July–August 04.
- Liddell, K., Newton, T., Adams, M., Muller, B., 2011. Energy consumption for Kell hydrometallurgical refining versus conventional pyrometallurgical smelting and refining of PGM concentrates. *J. S. Afr. Inst. Min. Metall.* 111 (2), 127.
- Liddell, K.S., Adams, M.D., 2012. Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates. *J. South Afr. Inst. Min. Metall.* 112 (1), 31–36.
- Lottering, M.J., Lorenzen, L., Phala, N.S., Smit, J.T., Schalkwyk, G.A.C., 2008. Mineralogy and uranium leaching response of low grade South African ores. *Miner. Eng.* 21 (1), 16–22.
- Mayze, R., 1999. An engineering comparison of the three treatment flowsheets in WA nickel laterite projects. In: *Proceedings ALTA Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum*.
- Mihaylov, I., 2003. Solvent extractants for nickel and cobalt: new opportunities in aqueous processing. *J. Miner., Metals, Mater. Soc.* 55 (7), 38–42.
- Mohammed, N., Ahmad, W.A., 2010. Application of Response Surface Methodology (RSM) for optimizing removal of Cr(VI) wastewater using Cr(VI)-reducing biofilm systems. In: *Proceedings of Regional Annual Fundamental Science Seminar 2010*.
- Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2014a. The extraction of Pt, Pd and Au from an alkaline cyanide simulated heap leachate by granular activated carbon. *Miner. Eng.* 55, 11–17.
- Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2014b. Evaluation of the Merrill-Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solutions. *Hydrometallurgy* 142, 36–46.
- Mpinga, C.N., Eksteen, J.J., Aldrich, C., Dyer, L., 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review. *Miner. Eng.* 78, 93–113.
- Muir, D.M., 2011. A review of the selective leaching of gold from oxidised copper–gold ores with ammonia–cyanide and new insights for plant control and operation. *Miner. Eng.* 24, 576–582.
- Navisa, J., Sravya, T., Swetha, M., Venkatesan, M., 2014. Effect of bubble size on aeration process. *Asian J. Sci. Res.* 7 (4), 482.
- Nayar, M.R., Watson, H.E., Sudborough, J.J., 2013. Reactions of chromates at high temperatures. Part 1. The synthesis and decomposition of calcium, sodium and magnesium chromates in air. *J. Indian Inst. Sci.* 7 (IV), 53–70.
- NEPC, 2004. Review of the Practicability of a 10 min Sulfur Dioxide Standard. National Environment Protection (Ambient Air Quality) Measure, Issues Paper March 2004.
- Norrgran, D.A., 1985. U.S. Patent No 4,541,993. U.S. Patent and Trademark Office, Washington, DC.
- Okamoto, H., 1990. The As-Pt (Arsenic-Platinum) system. *J. Phase Equilibria* 11 (5), 508–510.
- Parienyatwa, S., Escudero-Castejon, L., Sanchez-Segado, S., Hara, Y., Jha, A., 2016. Comparative study of alkali roasting and leaching of chromite ores and titaniferous minerals. *Hydrometallurgy* 165, 213–226.
- Pasandideh, S.H.R., Niaki, S.T.A., 2006. Optimizing multi-response statistical problems using a genetic algorithm. *Scientia Iranica* 13 (1), 50–59.
- Passos, C.G., Ribaski, F.S., Simon, N.M., dos Santos, A.A., Vaghetti, J.C., Benvenuto, E.V., Lima, É.C., 2006. Use of statistical design of experiments to evaluate the sorption capacity of 7-amine-4-azaheptylsilica and 10-amine-4-azadecylsilica for Cu(II), Pb(II), and Fe(III) adsorption. *J. Colloid Interface Sci.* 302 (2), 396–407.
- Prasad, M.S., Mensah-Biney, R., Pizarro, R.S., 1991. Modern trends in gold processing – overview. *Miner. Eng.* 4 (12), 1257–1277.
- Prasad, S., Pandey, B.D., 1998. Alternative processes for treatment of chalcopyrite — A review. *Miner. Eng.* 11 (8), 763–781.
- Prasad, S., Pandey, B.D., 1999. Sulphation roasting studies on synthetic copper-iron sulphides with steam and oxygen. *Can. Metall. Quart.* 38, 237–247.
- Qi, T.G., Liu, N., Li, X.B., Peng, Z.H., Liu, G.H., Zhou, Q.S., 2011. Thermodynamics of chromite ore oxidative roasting process. *J. Central South Univ. Technol.* 18, 83–88.
- Rambyana, R., Den Hoed, P., Garbers-Craig, A.M., 2014. Fire and brimstone: The roasting of a PGM concentrate. In: *The 6th International Platinum Conference*,

- 'Platinum-Metal for the Future'. The Southern African Institute of Mining and Metallurgy, pp. 2014.
- Rhoades, R.A., Bell, D.R., 2012. *Medical Physiology: Principles for Clinical Medicine*. Lippincott Williams & Wilkins.
- Rumiantsev, D.V., Popov, V.A., Tsemekhman, L.S., 2016. Development of a roasting process for arsenic gold-bearing concentrates to recover arsenic into a low-toxic product and produce calcine suitable for further processing. *J. Siberian Federal Univ. Eng. Technol.* 9 (6), 811.
- Safarzadeh, M.S., Miller, J.D., Huang, H.H., 2014. Thermodynamic analysis of the Cu-As-S-(O) system relevant to sulfuric acid baking of enargite at 473 K (200°C). *Metall. Mater. Trans. B* 45 (2), 568–581.
- Sceresini, B., 2005. Gold-copper ores. *Develop. Miner. Process.* 15, 789–824.
- Senanayake, G., 2004. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications. *Miner. Eng.* 17, 785–801.
- Sheridan, M.S., Nagaraj, D.R., Fornasiero, D., Ralston, J., 2002. The use of a factorial experimental design to study collector properties of N-allyl-O-alkyl thionocarbamate collector in the flotation of a copper ore. *Miner. Eng.* 15 (5), 333–340.
- Shin, Y.J., Chang, J.W., Kim, J.H., Park, B.H., Lee, K.Y., Lee, W.J., Chang, J.H., 2009. A dynamic simulation of the sulfuric acid decomposition process in a sulfur-Iodine nuclear hydrogen production plant. *Nucl. Eng. Technol.* 41 (6), 831–840.
- Sibrell, P.L., Atkinson, G.B., Walters, L.A., 1994. *Cyanide Leaching Chemistry of Platinum-Group Metals*. US Department of Interior, Bureau of Mines.
- Singh, K.K., Shenoy, K.T., Rao, H., Ghosh, S.K., 2011. Flow simulations of industrial scale agitated tanks. *BARC Newsletter* 8–15.
- Sohn, H.Y., Wadsworth, M.E., 2013. *Rate Processes of Extractive Metallurgy*. Springer Science & Business Media.
- Stange, W., 1999. The process design of gold leaching and carbon-in-pulp circuits. *J. S. Afr. Inst. Min. Metall.* 99 (1), 13–25.
- Stauter, J.C., Um, R.T., 1977. U.S. Patent N° 4,029,734. U.S. Patent and Trademark Office, Washington, DC.
- Tathavakar, V.D., Antony, M.P., Jha, A., 2005. The physical chemistry of thermal decomposition of South African chromite minerals. *Metall. Mater. Trans. B* 36 (1), 75–84.
- Teng, T.T., Low, L.W., Yusup, Y., 2012. *Heavy Metal Ion Extraction Using Organic Solvents: An Application of the Equilibrium Slope Method*. INTECH Open Access Publisher.
- Tinoco, R., Acevedo, A., Galindo, E., Serrano-Carreón, L., 2011. Increasing Pleurotus ostreatus laccase production by culture medium optimization and copper/lignin synergistic induction. *J. Ind. Microbiol. Biotechnol.* 38 (4), 531–540.
- Tshiongo, N., Mbaya, R.K.K., Maweja, K., Tshabalala, L.C., 2010. Effect of cooling rate on base metals recovery from copper matte smelting slags. *World Acad. Sci., Eng. Technol.* 4, 236–240.
- Udupa, M.R., 1982. Thermal decomposition of cerium (IV), cerium (III), chromium (III) and titanium (IV) sulphates. *Thermochim. Acta* 57 (3), 377–381.
- Ustaoglu, E., Geveci, A., 2007. Hot filtration: a way to enhance the recovery of chromite in sulfuric acid leaching, with or without the addition of perchloric acid. *Turk. J. Eng. Environ. Sci.* 30 (6), 375–380.
- Valenzuela, A., 2000. *Arsenic Management in the Metallurgical Industry*. PhD Thesis Université Laval, Quebec City, Quebec, Canada.
- Vermaak, C.F., 1995. *The Platinum-Group Metals: A Global Perspective*. Mintek, Randburg, South Africa.
- Walker, S.R., Jamieson, H.E., Lanzirotti, A., Hall, G.E.M., Peterson, R.C., 2015. The effect of ore roasting on arsenic oxidation state and solid phase speciation in gold mine tailings. *Geochem.: Explor. Environ., Anal.* 15 (4), 273–291.
- Wilburn, D.R., 2012. *Global Exploration and Production Capacity for Platinum-Group Metals from 1995 through 2015*.
- Wilkomirsky, I., 2014. *Dynamic simulation of processing high-arsenic copper concentrates in a fluidized bed roaster*. Presented at SME Annual Meeting/Exhibit, February 24–26, 2014, Salt Lake City, UT, USA.
- Yu, D., Utigard, T.A., Barati, M., 2012. Leaching behavior of the roasted nickel calcine. *Proceedings of the 51st Annual Conference of Metallurgists of CIM (COM 2012)*, Canada.
- Yu, D., Utigard, T.A., Barati, M., 2014a. Fluidized bed selective oxidation-sulfation roasting of nickel sulfide concentrate: Part I. Oxidation roasting. *Metall. Mater. Trans. B* 45 (2), 653–661.
- Yu, D., Utigard, T.A., Barati, M., 2014b. Fluidized bed selective oxidation-sulfation roasting of nickel sulfide concentrate: Part II. Sulfation roasting. *Metall. Mater. Trans. B* 45 (2), 662–674.
- Zhao, Y., Hou, Y., Cui, Y., Liang, H., Li, L., 2015. Recovery of copper from copper sulfide concentrate by sulfation roasting. *Int. J. Nonferrous Metall.* 4 (02), 9–13.
- Zolgharnein, J., Shahmoradi, A., 2010. Adsorption of Cr(VI) onto *Elaeagnus* tree leaves: statistical optimization, equilibrium modeling, and kinetic studies. *J. Chem. Eng. Data* 55 (9), 3428–3437.

**CHAPTER IV : SULFURIC ACID AND MOLTEN SALTS CHLORINATION
BAKE PROCESSES AT 650°C**

Submitted for publication as

Atmospheric leach process of high-chromitite PGM-bearing oxidized mineralized ore
through a single-stage and two-stage techniques.

Cleoplace Ngoie Mpinga, Jacques Eksteen, Chris Aldrich, Laurence Dyer., 2018.
Minerals Engineering 125, 165-175.

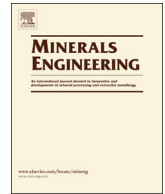
Accepted for publication on 04th May 2018.

© 2018 Elsevier Ltd.

Reprinted with permission from the publisher.

SUMMARY

The results of sulfation roast as well as molten salts chlorination roast carried out at 650°C are presented, followed by various aqueous processing options. Sulfation roast results at said temperature are investigated and compared to those obtained in Chapter III i.e. at 550°C.



Atmospheric leach process of high-chromitite PGM-bearing oxidized mineralized ore through a single-stage and two-stage techniques

Cleophae Ngoie Mpinga, Jacobus Johannes Eksteen*, Chris Aldrich, Laurence Dyer

Western Australian School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, GPO Box U1987, Perth 6845, Western Australia, Australia

ARTICLE INFO

Keywords:

Oxidized mineralization
Sperrylite
Chloride bake
Acid bake
Leaching
Platinum
Palladium

ABSTRACT

The fast depletion of sulfide PGM-bearing minerals and the deteriorating socio-political environments in most primary PGM producing countries have triggered interest in exploring the recovery of these metals from high-chromium PGM-bearing oxidized ores – sometimes contain relatively high marketable PGM values – which have proven to be more difficult to process by conventional metallurgical practice which involves grinding, milling, froth flotation into a sulfide concentrate, smelting and matte production and chemical refining.

This paper reports the results of an extensive evaluation campaign performed in both acidic sulfuric and chloride media. Leach tests were conducted in either a single-stage or a two-stage process and the results are compared and contrasted. Using a high-chromium PGM oxidized mineralized ore, the hybrid pyro-hydro-metallurgical and low-temperature single-stage salt chlorination process proved successful for simultaneously and efficiently leaching Cu, Ni, Pt and Pd without the need and/or addition of further oxidizing agents. The technique is expected to be a direct treatment route from flotation concentrate to PGM refinery feed.

Various chlorinating agents, including CaCl_2 , MgCl_2 , SnCl_2 and AlCl_3 , were tested. A CaCl_2 and MgCl_2 mixture acted synergistically for simultaneous dissolution of both Pt and Pd, achieving 99.7% Pt and 100% Pd recovery when thermally calcined at 650 °C, at a heating rate of 5.42 °C/minute for 6 h, and then leached at 90 °C for a minimum of 3 h in 6 M HCl. Copper and nickel extraction were lower but had not plateaued even after 24 h reaching 75.4 and 90.9% extraction respectively.

It was also observed that when MgCl_2 was used on its own, it dissolves more platinum than palladium, while the opposite was true using CaCl_2 . The leaching process was controlled by surface chemical reactions with a determined activation energy of 46 kJ/mol. The dissolution rate was limited by the ratio of HCl volume-to-solid content. The recovery mechanism of Pt from PtAs_2 and some recommendations for future prospects have been suggested.

1. Introduction

The fast depletion of sulfide PGM-bearing minerals and the deteriorating socio-political environments in most primary PGM producing countries have triggered interest in exploring the recovery of these metals from high-chromium PGM-bearing oxidized ores – sometimes contain relatively high marketable PGM values – which have proven to be more difficult to process by conventional metallurgical practice which involves grinding, milling, froth flotation into a sulfide concentrate, smelting and matte production and chemical refining (Sefako et al., 2017; Kraemer et al., 2015; Bulatovic, 2003).

In general, the processing of high-chromium oxidized ores by conventional flotation techniques typically results in very poor concentrate grade and PGM recoveries (Becker et al., 2014; Lewins and Greenaway, 2004; Bulatovic, 2003). Previous attempts to extract PGMs from such

ore type have proved uneconomic due to low recoveries ($\ll 50\%$) achieved by conventional metallurgical methods (Oberthür et al., 2013). Hence if an oxide ore cannot be preconcentrated, the method of treatment will have to accommodate large volumes of relatively low-grade material containing PGMs in a wide variety of mineral forms (Evans, 2002) that cause hydrometallurgical processes to be inappropriate. At present, oxide ores are either left *in-situ*, stockpiled or discarded as waste (Oberthür et al., 2013).

There has been some considerable research aimed at improving flotation recoveries of oxidized PGM ores by employing techniques such as (1) controlled potential sulfidization prior to flotation (Kalichini et al., 2017; Becker et al., 2014; Lee et al., 2009; Newell et al., 2006), (2) acid pretreatment of ores before flotation (Luszczkiewicz and Chmielewski, 2008) and (3) the use of various flotation reagent schemes (Becker et al., 2014; Lee et al., 2009; Bulatovic, 2003; Lee

* Corresponding author.

E-mail address: jacques.eksteen@curtin.edu.au (J.J. Eksteen).

<https://doi.org/10.1016/j.mineng.2018.05.007>

Received 20 December 2017; Received in revised form 22 April 2018; Accepted 4 May 2018
0892-6875/ © 2018 Elsevier Ltd. All rights reserved.

et al., 1998; Assis et al., 1996). Besides these techniques, direct leaching approaches have also been tested, where sperrylite has been found to be the main residual platinum bearing mineral remaining undissolved (Mpinga et al., 2017; Sefako et al., 2017; Mwase and Petersen, 2017; Kraemer et al., 2015).

This study follows on from earlier work by the same authors (Mpinga et al., 2017; Mpinga et al., 2015) where the investigation focus was to optimise the recovery of copper, nickel, platinum and palladium from a complex, chromite-rich Ni-Cu-PGM oxidized mineralized ore. This paper presents the results of exploratory research aimed at extracting these metals through either a single or a two-stage leach process. The results of sulfation roast as well as a salt chlorination roast are presented, followed by various aqueous processing options. Most of the emphasis was on the atmospheric pressure chlorination roast pretreatment followed by an acid chloride leach of the oxidized ore as it proved most effective. Emphasis was also placed on platinum (mineralized as sperrylite) due to its reputation of being more refractory towards oxidation/dissolution in comparison with other precious metals (minerals).

2. Theoretical background

2.1. Base metals beneficiation for exposing refractory PGMs

Base metals beneficiation associated with PGM ores in oxidized mineralization has been extensively reviewed by Mpinga et al. (2017). These authors outlined the significance of H₂SO₄ concentration on sulfation roast process prior to water leach. Their results revealed that most of the leaching occurred in the first 60 min (first data point) achieving 86% overall Ni extraction. A small increase of 4% was attained after 24 h and the curve plateaued at approximately 90%. In addition, only a low percentage of chromium and iron (10.40 and 13.60% in the ore, respectively) accompanies copper and nickel as water-soluble sulfates (0.80 and 1.46%, respectively).

However, the mineralogical characterization unfortunately still identified the presence of sperrylite in the water leach residues following the roast at 550 °C. To the best knowledge of the authors, chlorine gas is required to improve the extraction in a two-stage leach process (Liddell and Adams, 2012; Tatarnikov et al., 2004). PGM-bearing concentrates are leached under aggressive conditions in a HCl/Cl₂ medium (Sole et al., 2005). The HCl/Cl₂ leach approach is not suitable for low-grade ores or concentrates, but rather highly concentrated PGM feedstocks as found in PGM refineries. Therefore, the dissolution efficiency of refractory PGM minerals such as PtAs₂ might only be improved by thermal pretreatment processes supposed to influence the oxidation state of arsenic in the sulfide melt.

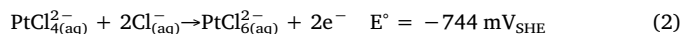
Hence instead of sulfation bake, a molten salt chlorination bake process performed at 650 °C, which lies just below the temperatures at which copper and nickel ferrites form (670 and 764 °C, respectively) and just above the temperatures (500–600 °C) at which PtAs₂ starts to decompose (Muir and Ariti, 1991; Okamoto, 1990) would be appropriate to volatilize and remove arsenic in the off-gas stream or as a calcium arsenate Ca₃(AsO₄)₂ compound. The sublimation point of arsenic is 613 °C (Dunn et al., 1995).

2.2. Thermodynamic considerations – minimum concentration of HCl as lixiviant

The Eh-pCl diagram (pCl being the negative logarithm of the Cl concentration) in Fig. 1 presents the stability regions of platinum chlorocomplexes. Their domain exists below the oxygen line and hence, from a thermodynamic viewpoint, the leaching of platinum metal is possible in chloride solutions containing oxygen. The diagram also shows that under high chemical potential of chloride ions, i.e. in the low pCl region, the complex ions PtCl₆²⁻ and PtCl₄²⁻ are more stable than Pt chlorides and Pt oxides (Horike et al., 2012). PtCl₆²⁻ predominates at

a wide area of acidic and high potential regions. This implies that chlorinated platinum can be dissolved in acidic chloride-ion-containing solutions without requiring a strong oxidant, as it is already present in an oxidized valent state.

The stability of PGM chlorocomplexes increases at higher chloride ion concentrations in solution, and this also increases their dissolution efficiency (Horike et al., 2012; Mahmoud, 2003). Baglin et al. (1985) emphasized that half reactions for their dissolution in chloride media are not dependent upon solution pH, but are strongly dependent on chloride concentration (Eqs. (1) and (2)). Dawson and Kelsall (2007) stated that it is usual practice when dissolving PGMs in acidic chloride media to use chloride concentrations of > 3 M, in order to increase their product solubilities and depress their equilibrium potentials.

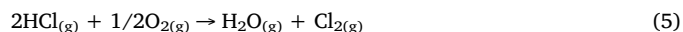
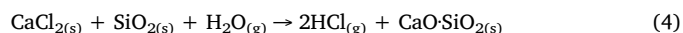
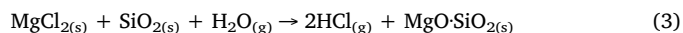


Industrial leach liquors generally contain up to 6 M HCl (Malik and Paiva, 2010). In this context, Nikoloski and Ang (2014) have observed that PtCl₆²⁻ predominates in acidic solutions when HCl is ≥ 3 M, while PdCl₄²⁻ dominates for concentrations of ≥ 0.1 M, and RhCl₆³⁻ is the prevailing species when HCl is ≥ 6 M. Although a standard potential higher than 730 mV_{SHE} (Eq. (1)) is required to oxidize Pt_(s), the rate of this reaction is far too slow for practical purposes (Benke and Gnot, 2002).

2.3. Molten salt chlorination roasting

It has been stated that following a salt fusion, platinum metals cannot be brought into solution, or can only be brought into solution with unsatisfactory yields without special measures (Schlecht, 1958). Among those measures, a requisite quantity of water may be added to facilitate increased physical contact between reactants in the roasting process (Han and Kim, 2006). Water is added such that the resulting mixture forms into a paste-like consistency (Mpinga et al., 2017; Han and Kim, 2006).

Molten salt chlorination roasts are typically carried out in the presence of moisture and in mildly reducing atmospheres. Moisture has been considered to be an essential component in the process for the production of HCl and/or Cl₂ (Eqs. (3)–(6)) by pyrohydrolysis of chloride salts under the catalysis of silica (Zhou et al., 2016). Chloride salts – preferably CaCl₂ or MgCl₂ – are chosen based on their low melting points and low vapour pressures as compared to the temperature (650 °C in this study) and the nature of the roasting reactor to be used.



The melting point of chloride salts varies significantly depending on their degree of hydration. It is as low as 30 °C for CaCl₂·6H₂O, while 772 °C for anhydrous CaCl₂; likewise MgCl₂·6H₂O is 117 °C and 714 °C for anhydrous MgCl₂. At molar ratio of 1:1, Venkatesh et al. (2016) found that MgCl₂/CaCl₂ eutectic melting occurs at 625 °C. Hence base and precious metals chlorination may occur through MgCl₂/CaCl₂ eutectic melt in the reaction product layers. According to Doná et al. (2009), Cl₂ is able to attack Pt surface to form PtCl₄ (Eq. (7)). Platinum chloride (PtCl₄) is the only chloride of platinum species that is soluble in water (Renner et al., 2001; Gee, 1920). Other PGM chlorides that could form during the roasting stage may include: PtCl₂, PtCl₃, PtCl₄ and PdCl₂ (Chusova and Semenova, 2008).



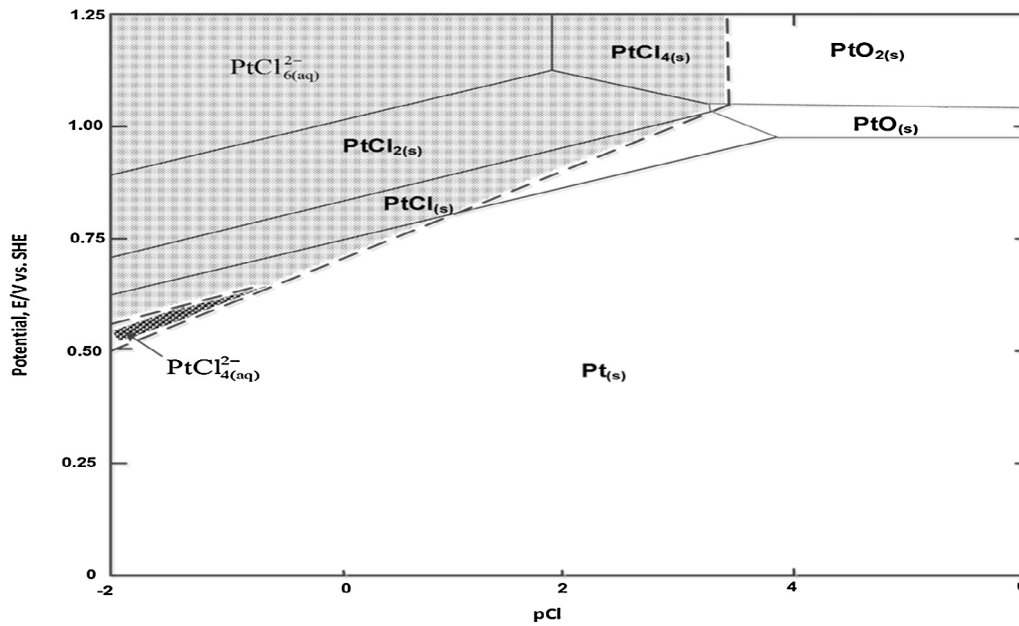


Fig. 1. Potential–pCl diagram for Pt–Cl–H₂O system at 25 °C and pH = 0. The value of pCl is defined as $pCl = -\log a_{Cl^-}$, $a_{i(s)} = 1$ (solid lines) and $a_{i(aq)} = 1$ (broken lines) (Horike et al., 2012).



However, the stable temperature ranges of Pt chlorides in the presence of Cl₂ gas are reported to be lower than 382 °C for PtCl₄, 382 to 450 °C for PtCl₃, and 435 to 515 °C for PtCl₂ (Horike et al., 2012). Above 380 °C, Renner et al. (2001) found out that PtCl₄ liberates chlorine and forms PtCl₂ (Eq. (8)), which is stable between 435 and 580 °C. According to Horike et al. (2012), PtCl₂ is produced by heating Pt metal in Cl₂ gas at 650 °C followed by cooling to 500 °C. The chlorination rate of platinum chloride formation is also dependent upon chlorine partial pressure (Landsberg and Schaller, 1971).

2.4. Mineral liberation and surface exposure

Direct cyanidation of ores and concentrates has been found effective only when precious metals were largely liberated in the earlier grinding stages (Green et al., 2004; Robins and Jayaweera, 1992). PGM minerals in chromite-rich materials such as UG-2 (Upper Group 2 reef in South Africa) and the Pantan Sill deposit (in Western Australia) have significantly smaller average grain sizes (3–11 μm) and require fine grinding for full liberation. Lottering et al. (2008) attempted to differentiate ore liberation and surface exposure. They pointed out that surface exposure was a very good indicator of the leachability, because only intrinsic kinetic inertness to leaching reagents can cause an exposed mineral to remain unleached.

2.5. Kinetics analysis – selection of a model – reaction controlling mechanism

Platinum dissolution being the rate limiting factor, the leaching kinetics was assessed by using the classical: (1) shrinking core model (SCM) and (2) shrinking spherical particle (SSP). According to the shrinking model, when a process is controlled by any of the mechanisms in Eqs. (9)–(13), its left side plotted versus time should give a straight line – assessed by using correlation coefficient (R²) values – where the slope is the leaching rate constant. Using the Arrhenius Equation (Eq. (14)) to determine the activation energy of the leaching process, the obtained reaction rate constants (displaying high correlation coefficient values) were plotted against the reciprocal of the absolute temperature.

$$\eta = kt \quad (\text{Liquid-film diffusion control: unchanging size}) \quad (9)$$

$$1-(1-\eta)^{2/3} = kt \quad (\text{Liquid-film diffusion control: changing size}) \quad (10)$$

$$1-3(1-\eta)^{2/3} + 2(1-\eta) = kt \quad (\text{Product layer diffusion control}) \quad (11)$$

$$1-(1-\eta)^{1/3} = kt \quad (\text{Surface chemical reaction control}) \quad (12)$$

$$(1/3)\ln(1-\eta) + \frac{1}{(1-\eta)^{1/3}-1} = kt \quad (\text{Mixed control}) \quad (13)$$

$$k = Ae^{-E_a/RT} \quad (14)$$

Taking the natural log of both sides of the Arrhenius Equation gives Eq. (15), where k = leaching rate constant, η = fractional conversion, t = leaching time, A = frequency factor (Arrhenius constant), E_a = activation energy (kJ/mol) of the dissolution reaction, R = gas constant (8.314 J/mol·K) and T = absolute temperature (K).

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad (15)$$

Asamoah-Bekoe (1998) calculated the activation energy of acid-soluble and chlorine soluble PGMs to be 23.05 and 42.36 kJ/mol, respectively. The reaction mechanisms were found to be generally chemical reaction controlled. This gives an idea of the order of magnitude of the expected activation energy in this study. A value of E_a over 40 kJ/mol implies charge transfer, chemical or surface-controlled processes (linear leaching), whereas an E_a of less than 40 kJ/mol suggests that the leaching process is controlled by diffusion (parabolic leaching) (Li et al., 2013). Generally, as argued by Crundwell (2013), the activation energy is below 20 kJ/mol for diffusion-controlled reactions, and it is above 40 kJ/mol for chemical-controlled reactions.

3. Materials and methods

3.1. Materials

3.1.1. Run-of-mine ore sample

The oxidized run-of-mine ore sample used in this study was from Pantan Sill Deposit. This is the same ore that was previously used and described by Mpinga et al. (2017). Its elemental and mineralogical compositions are displayed in Table 1. Unless otherwise noted, the P₈₀ mean size of particles fed to the roasting processes was either 30 or

Table 1
Chemical and mineralogical analyses of the high-chromite content ore in oxidized mineralization used in the roast-leach tests.

Chemical analysis		Mineralogical analysis	Content (%)
Elements	Content (%)	Major phases	
Fe	13.60	Chromite (FeCr ₂ O ₄)	78.12
Cr	10.40	Chlorite – Clinocllore	11.16
		[(Mg, Fe, Li) ₆ AlSi ₃ O ₁₀ (OH) ₈] –	
		[(Mg, Fe ²⁺) ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈]	
Mg	7.18	Minor phases	
Al	5.35	Olivine (Mg ²⁺ , Fe ²⁺) ₂ SiO ₄	3.23
Ca	0.42	Ferrotschermakite	1.95
		Ca ₂ [(Fe ²⁺ , Mg) ₃ Al ₂](Si ₆ Al ₂)O ₂₂ (OH) ₂	
Ti	0.3190	Pentlandite (Fe, Ni) ₉ S ₈	1.51
Na	0.0310	Ankerite [Ca(Fe, Mg, Mn) (CO ₃) ₂	0.91
Ni	0.31	Rammelsbergite (NiAs ₂)	0.80
Mn	0.23	Chalcopyrite (CuFeS ₂)	0.65
Zn	0.12	Magnesiogedrite	0.62
		[(Mg, Fe ²⁺) ₅ Al ₂ Si ₆ Al ₂ O ₂₂ (OH) ₂]	
Cu	0.0646	Hematite/Magnetite [Fe ₂ O ₃ /Fe ₃ O ₄]	0.25
Si	2.64	Columbite [(Fe, Mn)Nb ₂ O ₆]	0.23
S	0.78	Traces phases	
C	0.11	Bornite (Cu ₅ FeS ₄)	0.10
V	0.0609	Covellite (CuS)	0.02
Co	0.0314	Sperrylite (PtAs ₂)	0.02
As	0.0185	Chromiferite [Fe ₃ Cr _{1-x} (x = 0,6)]	0.02
Content (g/t)			
Pd	15.20		
Pt	12.80		
P	51.4		

64 µm. Prior to subsequent leaching processes, only the 64 µm calcined material was reground to P₈₀ of 16 µm.

3.1.2. Reagents and solutions

Analytical Reagent grade NaSCN (98%), SnCl₂ (98%), KI (99%), HCl (37%), H₂SO₄ (98%), CaCl₂·6H₂O (99%), MgCl₂·6H₂O (98%) and AlCl₃·xH₂O (95%) (used without further purification) were dissolved as required in distilled water to make up test solutions and/or used in mixtures fed to the roaster. In order to avoid ageing, all test solutions were freshly prepared on a daily basis.

3.2. Methods

A set of sixty tests were conducted to develop an effective process to extract base and precious metals from the oxidized run-of-mine ore in Table 1. Samples were subjected to a series of exploratory roasting and leaching tests aimed at identifying appropriate testwork parameters and to obtain estimates of their optimum dosage conditions. The experimental setup and procedures are the same as those described previously (Mpinga et al., 2017). The only difference was an increased roasting temperature of 650 °C instead of 550 °C and a shortened sulfation roasting time of 15 min instead of 2 h.

Chlorination roasting tests were conducted in a muffle furnace with specified amount of charge per batch, after mixing thoroughly for 5 min in a crucible the run-of-mine ore and chloride salts in a particular mass ratio. The calcination was conducted at 650 °C for up to 6 h in a covered crucible (not sealed) then cooled to room temperature inside the furnace, before being leached in 6 M HCl at 95 °C and 1 to 5%w/v for 24 h with mechanical agitation provided by an overhead sealed-shaft stirrer driven at 600 rpm. Any changes in variables are noted in the figures showing their effect. The influence of roasting time, leaching time, dosage of various chloride salts and hydrochloric acid on leaching rate of base and precious metals was investigated separately.

To prevent further reaction with the leached material which may have been carried over from the process, aliquots of 3 mL were collected at specific timed intervals through 0.45 µm pore size syringe filters, and analysed for dissolved metals by ICP-MS. The slurry was

filtered and the residue was washed thoroughly several times with distilled water to remove any physically attached ions or any unreacted ligands (reagents) and oven-dried at 110 °C for 24 h prior to chemical and mineralogical characterisations. Assuming no metal losses due to the formation of volatile chlorides, the percentage metal extraction (X_M) was estimated using Eq. (16), where m_t and m_f are the metal mass in the leaching solution at time t and the final solution, respectively; m_r is the metal mass in the final residue after leaching.

$$X_M = \frac{m_t}{(m_f + m_r)} \times 100 \quad (16)$$

4. Results and discussion

4.1. Exploratory sulfating roast-leach

Insights into the conditions needed for roasting were obtained by Mpinga et al. (2017). They reported sperrylite was still present in the leach residues when sulfated roasted at 550 °C. A higher roast temperature of 650 °C was investigated in this study to ensure sperrylite would decompose. This was based on the assumption that increasing the roast temperature above the As-Pt eutectic of 597 °C (Okamoto, 1990), would enable the arsenic to be released. Its concentration in the calcined ore was reduced from 185 to less than 0.5 g/t. Mineralogical examination confirmed sperrylite had decomposed (see Section 4.3).

Fig. 2 shows the extraction of base metals from the 650 °C, 15 min sulfate calcined ore. Cu and Ni were easily leached reaching > 85% in 1 h with final extractions of 99.0% and 92.1% respectively in 24 h. Pt and Pd showed poor dissolution (< 0.5%) while Fe and Cr dissolution was 12 and 3% respectively. A secondary leach was investigated to improve the extraction of Pt and Pd. The primary leach residue was leached in sulfuric acid with thiocyanate at 50 and 85 °C in the presence and absence of iodide as a catalyst (Fig. 3). Pt in all cases failed to leach (< 0.2%) and less than 40% of the Pd was extracted.

No matter the temperature, the extraction of palladium quickly plateaued after 4 h and lower extraction were observed in the presence of iodide. This poor performance was attributed to additional iron dissolution in the second leach (~45%) which is likely to have precipitated as a jarosite (iron hydroxide) (Broadhurst and Du Perez, 1993) and would possibly passivate the surface. Jarosite-type compounds have the ability to precipitate iron from acidic leach solutions (Dutrizac, 1983). The actual reason for the mixed ligand system performing poorly is unclear and requires further investigation.

Special attention should be paid to the recent complementary work by Shaik and Petersen (2017). They investigated the effectiveness of thiocyanate, cyanide and ferricyanide to act synergistically for extracting Pt from pure PtAs₂ specimen in both acidic and alkaline solutions. The use of pure mineral eliminated potential harmful interferences and ideally allowed to more accurately determine first-hand the rate and extent of platinum extraction only, prior to examining methods of treating low-grade and other complex platinumiferous materials.

In alkaline media, sperrylite was shown to be refractory with leaching efficiencies of < 10% under the combination of lixivants tested, i.e. 5.9 and 8.1% extraction were achieved respectively with CN⁻/Fe(CN)₆³⁻ and SCN⁻/CN⁻/Fe(CN)₆³⁻ systems within 30 h at 50 °C. On the other hand in acidic- SCN⁻ solution used on its own or combined with ferricyanide as an oxidant, sperrylite remained completely unleached, corroborating findings from this work. These results prove just how refractory PtAs₂ can be.

4.2. Exploratory molten salt chlorination roast-leach

4.2.1. Effect of residence time – reacted chloride

To improve the extraction of Pt and Pd, a chlorination roast-leach was investigated. Mixtures of CaCl₂, MgCl₂, SnCl₂ and AlCl₃ were added

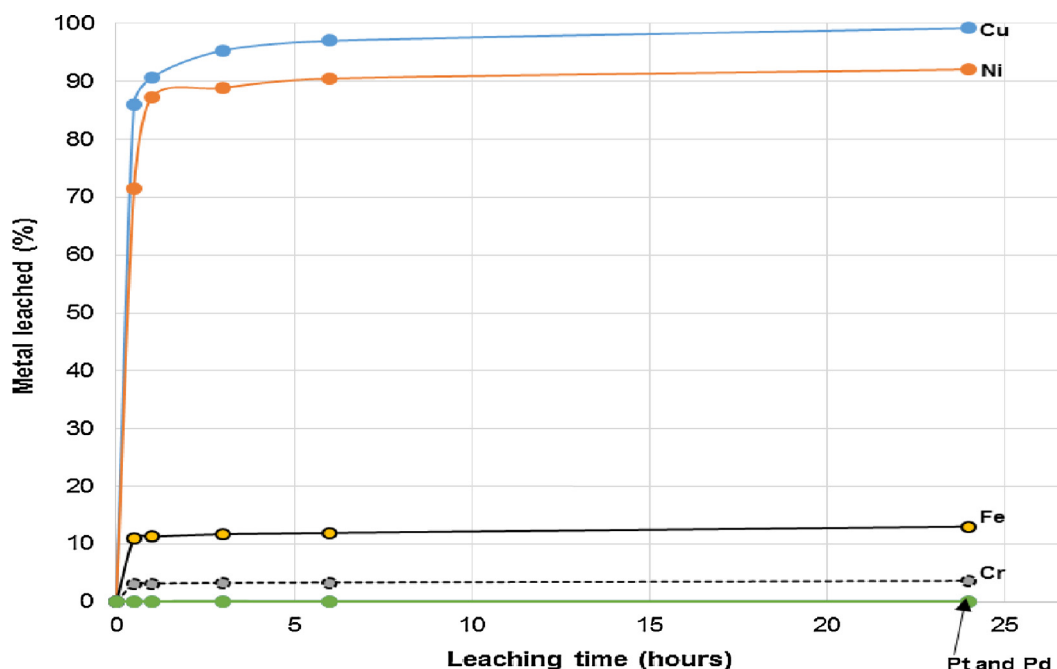


Fig. 2. Base metal leaching of sulfated ore in 1 M sulfuric acid at P_{80} 16 μm , 20% w/v solids, 95 °C and 600 rpm.

to the ore and roasted at 650 °C for different periods of time ranging from 15 min up to 6 h (Figs. 4 and 5). After calcination, the residues were leached in 6 M hydrochloric acid at 95 °C for 24 h. Note the calcines were allowed to cool inside the furnace, to ascertain the influence of roasting time on the conversion and extent of base and precious metals into their corresponding chloride salts and if any volatile components evolved.

Fig. 4 displays the leach results which showed increasing extraction of Pt and Pd with increasing reaction time. Cu showed the opposite response while Ni and Fe extraction showed little variation with roast residence time. Notably very little Cr (< 0.4%) was extracted. In some tests there were stains from volatile components on the crucible lid. The loss of chlorine is expected to result in less PtCl_4 (or PtCl_2) formation and this is the reason for poorer platinum extractions shown in Fig. 4.

Testing to gain a preliminary insight into the volatile behaviours of some species – especially chloride – involved in the roasting process,

thermal tests was carried out at 650 °C to quantify the amount of re-acted chloride and its magnitude loss. In such operations, mass losses are common. These may be assigned to: (I) the removal of physical and perhaps chemical water, (II) sulfur dioxide emission, (III) volatilisation of solid chlorides, or (IV) formation of intermediate products, etc.

To investigate chloride department, a mixture comprising 10 g ore + (15 g CaCl_2 + 15 g MgCl_2) was split into two fractions for roasting tests comparison. One fraction was left to dry in oven at 110 °C for 24 h to remove surface moisture. The other portion was thoroughly mixed in a tared crucible. This was weighed and transferred to the muffle furnace heated at 650 °C for 6 h. The calcine was then allowed to cool inside the furnace. Afterward the crucible was weighed and the percentage “mass loss” calculated as the ratio of weight loss to the initial weight of the sample. The dried and baked materials were ground using a mortar and pestle. Samples of both fractions were analysed by XRF.

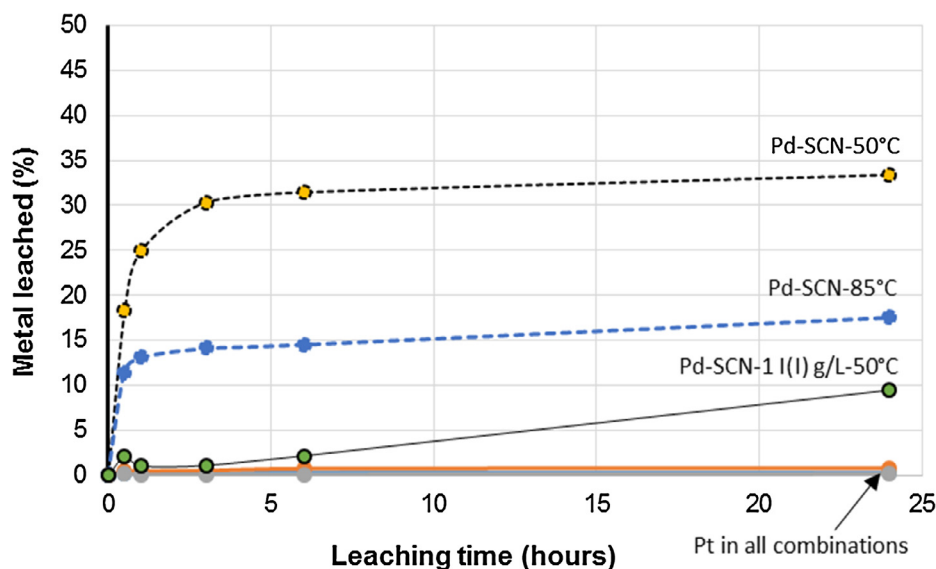


Fig. 3. Precious metal extraction from secondary leach in 40 g/L SCN^- , pH 2, oxygen flowrate 0.1 mL/min, 5% w/v solids and 600 rpm (note variations are noted in figure captions).

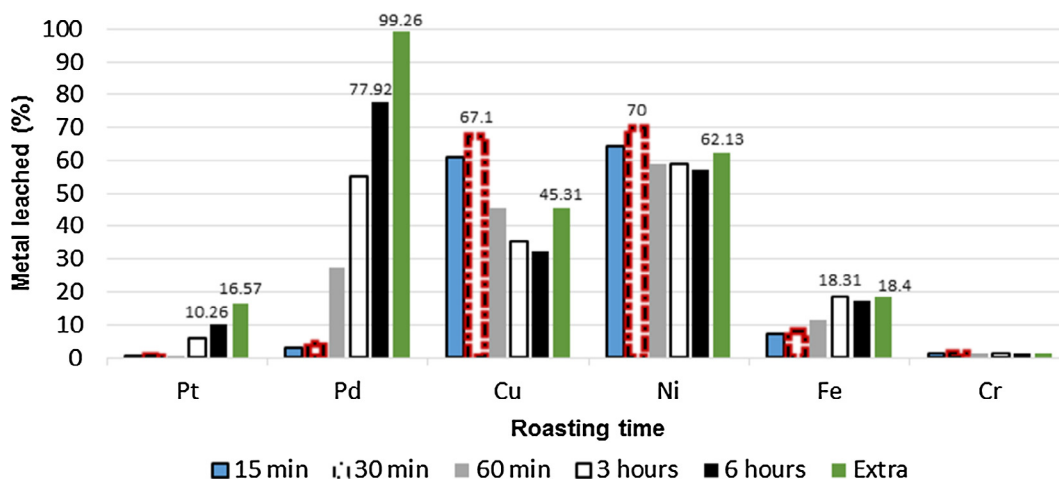


Fig. 4. Effect of roasting time on base and precious metal extraction leached in 6 M HCl at 1% w/v, 95 °C and 600 rpm with spiked 1 g/L SnCl₂ (Roast was 500 kg/t CaCl₂). “Extra” denotes ore blended with 500 kg/t CaCl₂ + 40 kg/t SnCl₂ and roasted at 650 °C for 3 h, then the reground calcine was leached in 6 M HCl only [without Sn(II) addition] for 24 h.

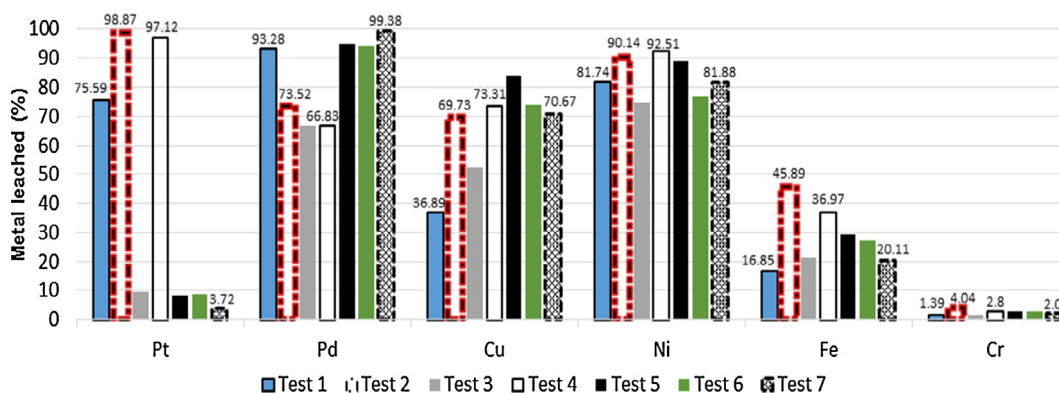


Fig. 5. Effect of residence time and chloride salt addition on base and precious metal extraction leached in 6 M HCl at 1% w/v, 95 °C and 600 rpm. Test 1 denotes ore blended with 3 t CaCl₂/t ore and roasted at 650 °C for 6 h. Test 2 denotes ore blended with 3 t MgCl₂/t ore and roasted at 650 °C for 6 h. Test 3 denotes ore blended with 3 t CaCl₂/t ore and roasted at 650 °C for 3 h. Test 4 denotes ore blended with 3 t MgCl₂/t ore and roasted at 650 °C for 3 h. Test 5 denotes ore blended with 3 t AlCl₃/t ore and roasted at 650 °C for 3 h. Test 6 denotes ore blended with 3 t AlCl₃/t ore and roasted at 650 °C for 6 h. Test 7 denotes ore blended with 1 t AlCl₃/t ore roasted at 650 °C for 3 h.

Table 2

Elemental composition change of some selected species from fresh and molten salts chlorination mixtures comprising 10 g ore + (15 g CaCl₂ + 15 g MgCl₂). Roasting conditions: 650 °C for 6 h at a heating rate of 5.42 °C/minute.

Element	Cl	Ca	Mg	Fe	Al	Cu	Ni	Cr	
Content (%)	0 h	35.4	9.96	9.95	13.6	5.35	0.065	0.310	10.4
	6 h	25.8	14.6	14.2	16.0	6.35	0.073	0.352	13.2

At the end of 6 h heat treatment and taking into account the amount (subtracted) of surface water, an overall mass loss of ~20% was recorded. Table 2 summarizes the mass changes of some selected species during the roasting. According to the chloride mass-balance, only 73% of it remained in the calcine product, i.e. some reacted; while the remaining 27% constitutes a significant loss (probably through Eqs. (3)–(5)), given the overall amount of chloride salts supplied.

4.2.2. Effect of chloride salt

To obtain evidence that may support the formation of platinum chlorides, excess amounts of chlorinating agent ranging up to 3 times the ore mass were applied to drive the chlorination reaction (Eq. (7)) to the right and to ensure complete metal chlorination. As can be seen from Fig. 5, the extent of Pt chlorination varied depending on the chlorinating agent and the residence time. High extractions of copper

and nickel and moderate percentages of iron were also extracted over the testing regime.

A six hour roast using CaCl₂ had the advantage of extracting acceptable amount of Pt (75.59%) and Pd (93.28%) while avoiding excessive iron dissolution (16.85%). The roast with CaCl₂ for 3 h translated in poor platinum and palladium extractions, i.e. 9.60 and 66.86% respectively after 24 h leach. No significant difference was observed when MgCl₂ was used in 3 or 6 h roast, both cases giving high iron dissolution, and achieved platinum extraction exceeding the 95% mark. AlCl₃ proved to be an adequate chlorinating agent for palladium only, with extractions exceeding 90% for both 3 and 6 h roast.

It was anticipated that the combination of raw ore, CaCl₂ and MgCl₂ mixture roasted at 650 °C for 6 h would act synergistically for simultaneous dissolution of both Pt and Pd. Such tests were performed and the results are summarized in Fig. 6. The extractions of Pt and Pd are both close to 100% (Test 1). The dissolution of chromium was minimal (1.62%), whereas iron reported to solution in relatively high concentration (38.6%).

At this stage there isn't information available to speculate on the mechanisms taking place through the abovementioned synergy. Thereby, further investigation in this direction would appear to be warranted (Mpinga and Eksteen, 2018). In addition, it is unclear as to which of the specific roasting factors (roasting time, roasting temperature and chlorinating agents' dosage), the leaching efficiency of

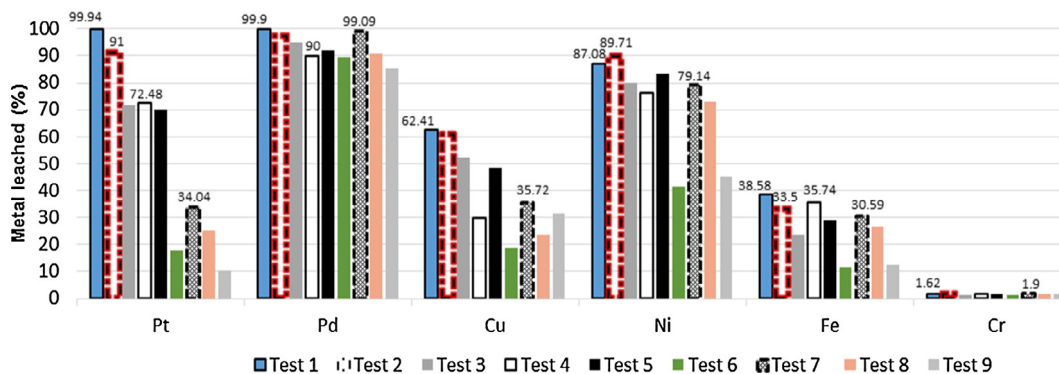


Fig. 6. Effect of CaCl₂ and MgCl₂ addition on base and precious metal extraction leached in 6 M HCl at 1% w/v, 95 °C and 600 rpm. Tests 1, 2 and 3 denote ore blended with (1.5 t CaCl₂ + 1.5 t MgCl₂)/t ore and roasted at 650 °C for 6 h, then leached in 6, 3 and 1 M HCl respectively. Tests 4, 5 and 6 denote ore blended with (500 kg CaCl₂ + 500 kg MgCl₂)/t ore and roasted at 650 °C for 6 h, then leached in 6, 3 and 1 M HCl respectively. Tests 7, 8 and 9 denote ore blended with (250 kg CaCl₂ + 250 kg MgCl₂)/t ore and roasted at 650 °C for 6 h, then leached in 6, 3 and 1 M HCl respectively.

both copper and nickel are correlated to. Their incomplete leaching may be attributed to the phase transformations occurring during heat treatment of the spinel host, which ultimately determines their maximum attainable extractions.

4.2.3. Effect of HCl concentration on platinum and palladium leaching from calcines

The effect of HCl concentration on platinum and palladium leaching from chlorinated calcines is displayed in Fig. 6. Platinum showed a larger decrease in extraction compared to palladium as HCl concentration was decreased from 6 to 1 M. The platinum extraction also decreased significantly with decreasing chloride salt content in the roast. The decrease in chloride concentration due to CaCl₂/MgCl₂ starvation, probably decreased the availability of Cl_{2(g)} on the basis of Eqs. (3)–(5), which accordingly decreased platinum conversion percentage according to Eq. (7).

4.2.4. Effect of leaching time

Simultaneous use of CaCl₂ and MgCl₂ played a significant role in catalysing the chlorination process. The results demonstrated (Fig. 7) that the dissolution of palladium was fast and the endpoint was reached within 30 min (first data point) as compared to platinum, which needed slightly prolonged leaching time of 3 h to reach maximum extraction.

The results also suggested that prolonging the leach time beyond 6 h was unnecessary. Hence, 6 h was adopted as maximum recovery time to ensure complete extraction. In all leach residues, Pt and Pd remained well below the analytical detection limit offered by fire assay.

Prior to chlorination roast, the ore was ground to P₈₀ of 30 μm, therefore the chlorinated calcine was leached without additional re-grinding. In this way, an assessment of the combined effect of mineral liberation and surface exposure was attempted.

4.2.5. Effect of leaching temperature

To determine the influence of temperature on PGMs solubilization, leaching tests were performed at four different temperatures: 25, 50, 75 and 90 °C. Each dissolution experiment was conducted for 24 h at an agitation rate of 600 rpm. The solid-to-liquid ratio was kept constant at 5%w/v. Unlike ambient temperature palladium leaching processes, platinum dissolution rate increased with an increase in temperature. This may be due to the thermal stability of platinum chlorocomplexes (Hernandez and Choren, 1983).

The results also showed only slight difference between samples leached at 75 and 90 °C. It is worth noting that a temperature of 70 °C is industrially practiced by Impala Platinum Metal Refinery for optimal leaching (Asamoah-Bekoe, 1998), presumably as a reasonable compromise between acid loss through evaporation and metal dissolution.

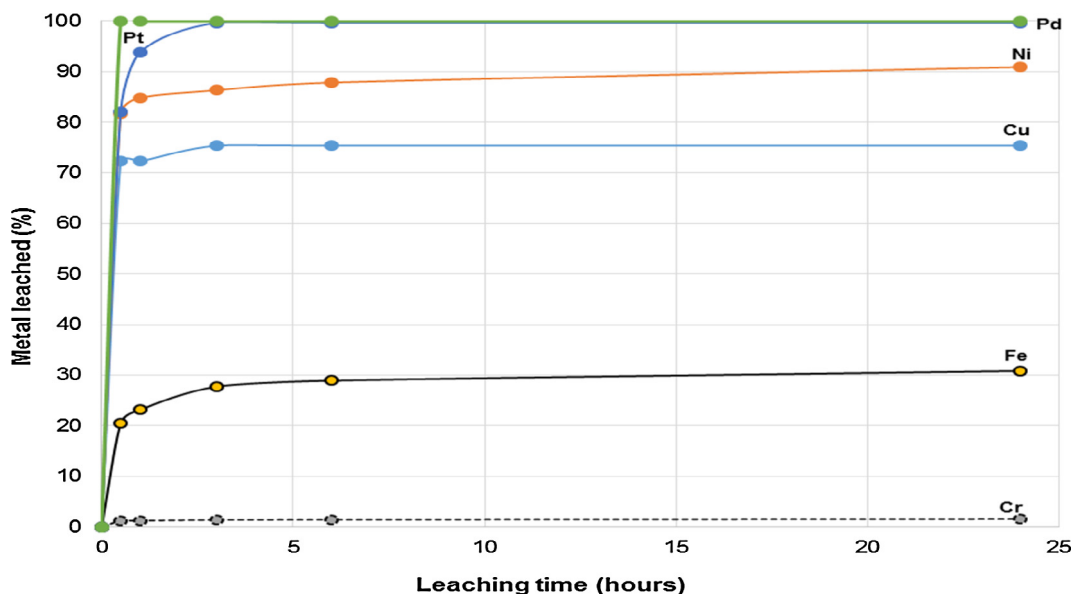


Fig. 7. Extraction of base and precious metal leached in 6 M HCl at 5% w/v, 90 °C, P₈₀ 30 μm and 600 rpm (calcination with CaCl₂/MgCl₂ 1:1, 3 t/t ore).

Table 3

Extent of PGMs transfer into solution at various solid-to-liquid ratios, after 6 h leach at 90 °C in 6 M HCl. Molten salts chlorination of the mixture comprised 1 ton ore + 1.5 ton CaCl₂ + 1.5 ton MgCl₂ roasted at 650 °C for 6 h and a heating rate of 5.42 °C/minute.

Solid-to-liquid ratio (%w/v)	Extent of PGMs transfer into solution (%)	
	Pt	Pd
1	99.80	100
5	99.71	100
10	41.06	100
25	0	5.07

Therefore, the optimum operation temperature should be decided in industry operations.

4.2.6. Effect of stirring speed

The influence of stirring speed on PGMs leaching was studied at 140, 280, 420 and 600 rpm in solution containing 6 M HCl at 90 °C and 5%w/v pulp density. The dissolution of platinum and palladium at these stirring speeds was almost 100% within 3 h. The leaching kinetics did not appear sensitive to agitation speed, i.e. diffusion control played an insignificant role in the process. However, in all subsequent experiments, the stirring speed was kept at 600 rpm to be sure that mineral particles were brought into adequate contact with leaching reagents, which eliminates internal and external mass-transfer resistances.

4.2.7. Effect of solid-to-liquid ratio

As solid-to-liquid ratio ranged from 1 to 25%w/v (Table 3), the dissolution of both platinum and palladium decreased from approximately 100% to 0 and 5.07%, respectively; which was due to the gradual decrease of residual acid concentration. In other words, the decreased extraction was caused by the decrease of acid available per unit of solid. From the results given, 5%w/v was considered as the optimal pulp density.

The relative concentration of most relevant species in the leachate generated in the experimental program at 5%w/v solid-to-liquid ratio is displayed in Table 4. PGM concentrations are very low as compared to the elevated concentrations in leach liquors from UG-2 concentrate (59.4 mg/L Pt and 37.2 mg/L Pd) reported by Green et al. (2004) or 62.5 g/L Pt and 31.85 g/L Pd from Impala plant leach tests reported by Asamoah-Bekoe (1998). As such from an economic point of view, it is therefore imperative to leach a concentrate instead of the raw run-of-mine ore.

4.3. Chemical and mineralogical characterization

To identify chemical-mineralogical changes brought by the molten salt chlorination-leach tests, fresh raw ore, chlorinated calcines and solid leach residues were analysed by means of XRF, XRD, SEM and/or Tescan Integrated Mineral Analysis (TIMA GM Model) operated by the

Table 4

Relative concentration of most relevant species in the leachate generated in the experimental program at solid-to-liquid ratio of 5%w/v, leaching temperature of 90 °C after 6 h extraction in 6 M HCl.

Species	Content (µg/L)	Species	Content (mg/L)	Species	Content (mg/L)
Pt	639	Ca	20,300	As	5.5
Pd	760	Mg	11,800	P	5
Ag	20	Fe	2040	Sn	4.4
Au	16	Al	1340	Co	3.5
Ni	140,000	Cr	68	Zn	0.5
Si	90,000	S	75	Cu	23.5

Table 5

Quantitative X-ray diffraction of phases (%) present after various treatments.

Mineral	ROM	ROM at 650 °C without any reagent addition	1 ton ore + 1.5 ton CaCl ₂ + 1.5 MgCl ₂ at 650 °C for 6 h*	Leach residue at 5%w/v
Spinel group	82	88	51	99
Chlorite group	11	–	–	< 1
Brucite group	–	–	17	–
Olivine group	3	7	32	–
Vermiculite	–	5	–	–

(–) denotes undetected, (*) Sample was wet and required drying prior to analyses.

John de Laeter Centre at Curtin University.

It was shown that thermal treatment significantly changes the ore structure. New phases were observed even on simply heating the ore at 650 °C without any reagent addition (Table 5). Owing to the highly hygroscopic nature of charges (physically observed) to quantitative X-ray diffraction (QXRD) analysis, large numbers of unidentified peaks were observed, as such results in Table 5 should be regarded as indicative.

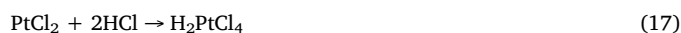
SEM examination also confirmed that new phases or solid solutions formed during the tests. Backscattered electron micrograph of the raw ore in Fig. 8A shows light grey areas corresponding to chromite mineral, whereas the dark grey are siliceous gangue.

However, the molten-like morphology of the calcine salt product in Fig. 8B and 8C as well as the leach residue (Fig. 8D) showed the formation of new products (new solid phases) attributable to the decomposition and reordering of the ore spinel structure to accommodate atoms that comprise the reaction products (Table 5).

It can also be seen (Fig. 8C) that the main reaction product formed during the chlorination process is composed of two distinct textural patterns (variants) with dense chromite particles removed from the spinel structure (Light grey areas) in association with other Mg, Ca, Al, Cl, etc. (Dark grey areas) intimately mixed in solid solutions.

4.4. Plausible reaction mechanism

In contrast to Mwase and Petersen (2017)'s assumption of the oxidation states of Pt and As in PtAs₂, which they assumed to be Pt⁽²⁺⁾As⁽³⁻⁾, Bai et al. (2017) stated that the formal oxidation state of Pt in sperrylite is 4+ and that of As is 2-; however, the As oxidation state in the sulfide melt may be different. Hence based on the above analyses and observation, a plausible reaction mechanism is that the *in-situ* generated Cl₂ attacks Pt surface to form PtCl₄ shown in Eq. (7). PtCl₄ is reported to dissociate on cooling to form PtCl₂ and Cl₂ (Eq. (8)). Regarding chemical leaching, literature reports that PtCl₄²⁻ forms mainly in aqueous chloride solutions (Eq. (17)), while PtCl₆²⁻ forms (Eq. (18)) in chloride solutions (Mpinga et al., 2015; Sun et al., 2015; Pospiech, 2012).



The residual free chlorine content present in the roasted product is expected to (1) provide high oxidation potential, and more importantly (2) to saturate the leaching solution (with chlorine), thereby converting tetrachloroplatinic(II) acid, H₂PtCl₄ to hexachloroplatinic acid H₂PtCl₆ (Gulliver and Levason, 1982). The possibility of forming Pt-M alloys (where M = Ca, Mg, Ba, Ni, Fe and/or Cu) during the roasting process can be completely excluded, as the experimental conditions were not sufficiently reducing (Horike et al., 2012; Yeates and Somorjai, 1983). Thus, the hypothesized mechanism is schematically described in Fig. 9.

Since the predominant species of platinum in the leaching solution under investigation is expected to be PtCl₆²⁻, which is more readily extractable by weak-base anion exchange resins as exploited by Mpinga

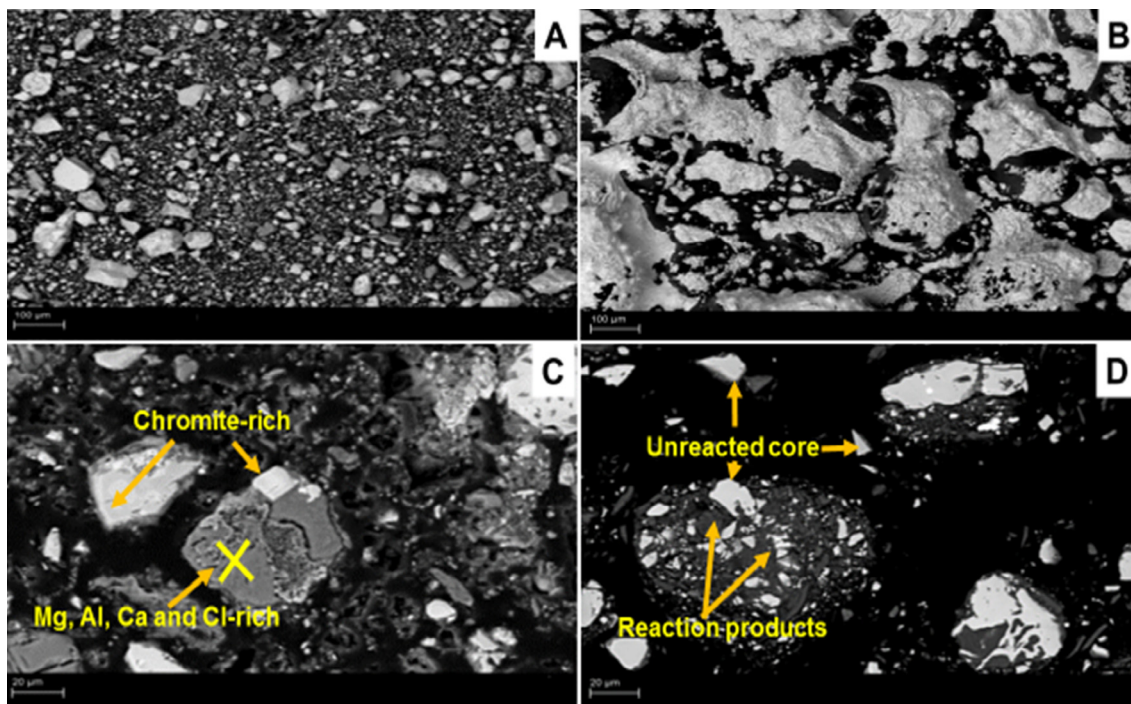


Fig. 8. (A) Backscattered-electron image of untreated fresh run-of-mine ore showing chromite grains (Light grey areas) and siliceous gangue (Dark grey areas); (B) Molten-like morphology of the 650 °C chlorinated ore reaction product before leaching; (C) Cross-sectional analysis of individual particles from figure (B); (D) Cross-sectional analysis of individual particles of ore residue after atmospheric leaching in 6 M HCl at solid-to-liquid ratio of 5%w/v, without the need and/or addition of oxidizing agents.

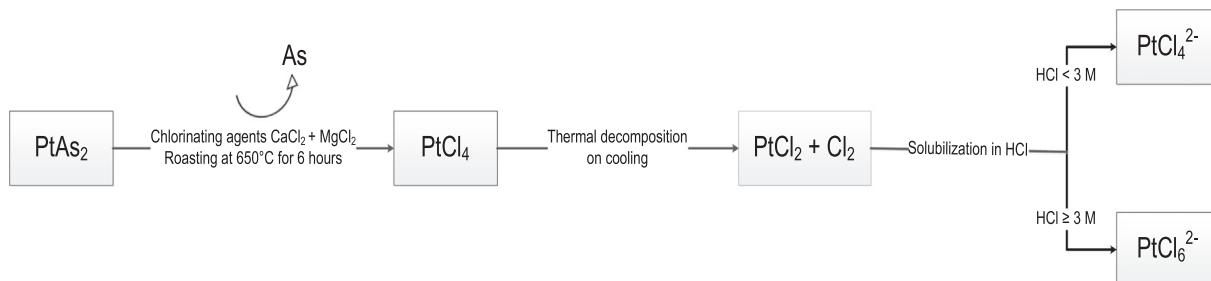


Fig. 9. Hypothesized recovery mechanism of platinum from PtAs₂ contained in oxidized mineralized ore.

Table 6

Values of apparent rate constants (expressed in h⁻¹) and correlation coefficients (R²) of five kinetics models at different temperatures and stirring speed.

Temperature (K) [#]	$\eta = kt$		$1-(1-\eta)^{2/3} = kt$		$1-3(1-\eta)^{2/3} + 2(1-\eta) = kt$		$1-(1-\eta)^{1/3} = kt$		$(1/3)\ln(1-\eta) + \frac{1}{(1-\eta)^{1/3}-1} = kt$		
	k	R ²	k	R ²	k	R ²	k	R ²	k	R ²	
298	9.10 ⁻⁵	0.63	7.10 ⁻⁵	0.83	4.10 ⁻⁵	0.71	4.10 ⁻⁵	0.96	13.10 ⁻⁴	0.53	
323	1.10 ⁻⁴	0.78	2.10 ⁻⁴	0.71	2.10 ⁻⁴	0.89	3.10 ⁻⁴	0.99	16.10 ⁻⁴	0.85	
348	2.10 ⁻⁴	0.70	4.10 ⁻⁴	0.82	5.10 ⁻⁴	0.83	7.10 ⁻⁴	0.94	18.10 ⁻⁴	0.32	
368	3.10 ⁻⁴	0.30	5.10 ⁻⁴	0.85	7.10 ⁻⁴	0.32	12.10 ⁻⁴	0.98	20.10 ⁻⁴	0.86	
Stirring speed (rpm)^{##}											
150	1.10 ⁻⁴	0.84	2.10 ⁻⁴	0.86	4.10 ⁻⁴	0.85	9.10 ⁻³	0.94	2.10 ⁻⁴	0.87	
280	2.10 ⁻⁴	0.77	3.10 ⁻⁴	0.80	5.10 ⁻⁴	0.78	7.10 ⁻³	0.95	5.10 ⁻⁴	0.42	
420	3.10 ⁻⁴	0.70	5.10 ⁻⁴	0.89	7.10 ⁻⁴	0.62	8.10 ⁻³	0.91	9.10 ⁻⁴	0.62	
600	4.10 ⁻⁴	0.70	6.10 ⁻⁴	0.91	8.10 ⁻⁴	0.62	1.10 ⁻²	0.98	18.10 ⁻⁴	0.86	

(#) denotes tests performed at 600 rpm, (##) denotes tests performed at 90 °C.

et al. (2018). These authors not only quantitatively extracted trace amounts of PGMs in the presence of huge concentrations of Fe(III) and other common accompanying non-ferrous metal ions, but also successfully eluted the loaded resin with only few bed volumes (2–4), resulting in a small volume of highly concentrated PGMs eluate which is

suitable for downstream processing.

4.5. Rate controlling step – activation energy

The dissolution process of platinum was described by fitting the

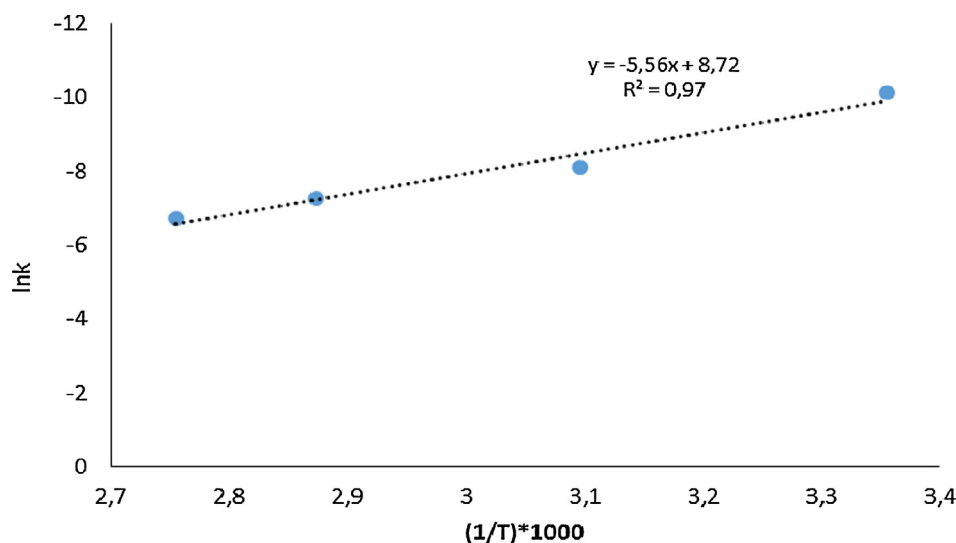


Fig. 10. Arrhenius plot for platinum leaching in 6 M HCl, slurry density of 5%w/v, stirring speed of 600 rpm, particle size distribution of 80% passing 30 μm .

shrinking model (Eqs. (9)–(13)) to the kinetic data. From the slopes, different rate constant (k) values were calculated (Table 6).

An Arrhenius plot was constructed to determine the activation energy of the process (Fig. 10). It was found that the activation energy of platinum dissolution at 5%w/v in 6 M HCl to be 46 kJ/mol, indicating a surface chemical controlled mechanism.

5. Conclusions

A detailed experimental program was undertaken to solubilize Cu, Ni, Pt and Pd from a PGM-bearing chromite ore from an oxidized mineralization. Two treatment routes including single-stage and two-stage leach are presented in this paper. The hybrid pyrohydrometallurgical and low-temperature single-stage molten salt ($\text{CaCl}_2/\text{MgCl}_2$) chlorination technique proved successful for simultaneously and efficiently enable leaching of all target metals without the need and/or addition of further oxidizing agents. Using cheap and readily available reagents (routinely used for snow and ice control on roadways), the process typically entailed roasting operation at 650 $^\circ\text{C}$ for 6 h residence time, resulting in almost complete chlorination with the formation of intermediate PGM products which further react with aqueous HCl to give chlorocomplex ions in solution.

For an optimum performance, the key success of the process resides in roasting in a specially designed reactor (e.g. an atmospheric pressure reactor that is at least well sealed) to enhance the dispersion of the *in-situ* generated Cl_2 into the cured ore. Such reactor would need to have the option to control the extent of chlorination achieved. Pyrohydrolysis of chloride salts and chlorine partial pressure were both important factors in the leaching reaction of PGMs. Using intermediate crushed ore ($P_{80} = 30 \mu\text{m}$), excellent leach beneficiation was achieved averaging 99.71% Pt and 100% Pd with relatively low co-extraction of deleterious chromium (0.31%). Therefore, it appears high Cr content can be allowed in the flotation concentrate without adversely affecting PGM recovery.

Treatment of concentrates is highly recommended in preference to raw run-of-mine ore for increasing PGMs concentration in the leachate to a level that would be more attractive for commercial applications. Ideally the technique can use a rougher flotation product at high mass pull e.g. 10% as compared to the usual 2% – a considerable amount of ore weight will be rejected – thus reducing separation costs and saving valuable minerals (e.g. sperrylite) that may be lost during further cleaner stages. Grinding finer than 30 μm was not necessary. With the development of this technique, substantial PGM recoveries from oxide and mixed oxide/sulfide ores are now possible. The technique is

expected to be a direct treatment route from flotation concentrate to PGM refinery feed.

The dissolution rate of PGMs is high enough to be considered for practical implementation in agitated reactors. These can be recovered from the pregnant solution, preferably before copper and nickel, by using highly PGM selective ion-exchangers. Resin-in-pulp (RIP) would be an attractive option, in order to avoid the solid/liquid separation and the unavoidable soluble losses of PGMs. The addition of SCN^- to the iron chloride containing leachate (ligand exchange reaction) serves as a preconcentration step for trace PGM components prior to their recovery, and enhances the formation of various ferric cationic complexes that are not extractable by anion exchange resins.

Acknowledgements

The research was sponsored by Panoramic Resources Ltd and the Minerals Research Institute of Western Australia (MRIWA Grant M458). Their financial support and permission to publish the results are kindly acknowledged with appreciation. The authors are also grateful for the financial support provided by the Curtin International Postgraduate Research Scholarships (CIPRS) at Curtin University, in Perth, Western Australia.

References

- Asamoah-Bekoe, Y., 1998. Investigation of the Leaching of the Platinum-group Metal Concentrate in Hydrochloric Acid Solution by Chlorine (MSc Thesis). University of the Witwatersrand, South Africa.
- Assis, S., Montenegro, L., Peres, A., 1996. Utilisation of hydroxamates in minerals froth flotation. *Miner. Eng.* 9 (1), 103–114.
- Baglin, E.G., Gomes, J.M., Carnahan, T.G., Snider, J.M., 1985. Recovery of platinum, palladium, and gold from Stillwater Complex flotation concentrate by a roasting-leaching procedure. *Complex Sulfides-Processing of ores, concentrates and by-products*, San Diego, California, 10–13.
- Bai, L., Barnes, S.J., Baker, D.R., 2017. Sperrylite saturation in magmatic sulfide melts: implications for formation of PGE-bearing arsenides and sulfarsenides. *Am. Mineral.* 102 (5), 966–974.
- Becker, M., Wiese, J., Ramonotsi, M., 2014. Investigation into the mineralogy and flotation performance of oxidised PGM ore. *Miner. Eng.* 65, 24–32.
- Benke, G., Gnot, W., 2002. The electrochemical dissolution of platinum. *Hydrometallurgy* 64, 205–218.
- Broadhurst, J.L., Du Perez, J.G.H., 1993. A thermodynamic study of the dissolution of gold in an acidic aqueous thiocyanate medium using iron (III) sulphate as an oxidant. *Hydrometallurgy* 32 (3), 317–344.
- Bulatovic, S., 2003. Evaluation of alternative reagent schemes for the flotation of platinum group minerals from various ores. *Miner. Eng.* 16 (10), 931–939.
- Chusova, T.P., Semenova, Z.I., 2008. Thermodynamics of the Pt-Cl system. *Thermochim. Acta* 469 (1), 59–64.
- Crundwell, F.K., 2013. The dissolution and leaching of minerals: mechanisms, myths and

- misunderstandings. *Hydrometallurgy* 139, 132–148.
- Dawson, R.J., Kelsall, G.H., 2007. Recovery of platinum group metals from secondary materials. I. Palladium dissolution in iodide solutions. *J. Appl. Electrochem.* 37 (1), 3–14.
- Doná, E., Cordin, M., Deisl, C., Bertel, E., Franchini, C., Zucca, R., Redinger, J., 2009. Halogen-induced corrosion of platinum. *J. Am. Chem. Soc.* 131 (8), 2827–2829.
- Dunn, J.G., Ibrado, A.S., Graham, J., 1995. Pyrolysis of arsenopyrite for gold recovery by cyanidation. *Miner. Eng.* 8 (4), 459–471.
- Dutrizac, J.E., 1983. Factors affecting alkali jarosite precipitation. *Metall. Trans. B* 14 (4), 531–539.
- Evans, D.M., 2002. Potential for bulk mining of oxidized platinum-group element deposits. *Appl. Earth Sci.* 111 (1), 81–86.
- Gee, G.E., 1920. Recovering Precious Metals from Waste Liquid Residues: A Complete Workshop Treatise Containing Practical Working Directions for the Recovery of Gold, Silver, and Platinum from Every Description of Waste Liquids in the Jewellery, Photographic, Process Workers, and Electroplating Trade. E. & FN Spon.
- Green, G., Smit, B.R., Maumela, D.M.C., Coetzer, H., 2004. Leaching and recovery of platinum group metals from UG-2 concentrates. *J. South Afr. Inst. Min. Metall.* 104 (6), 323–331.
- Gulliver, D.J., Levason, W., 1982. The chemistry of ruthenium, osmium, rhodium, iridium, palladium and platinum in the higher oxidation states. *Coord. Chem. Rev.* 46, 1–127.
- Han, K.N., Kim, P.N.S., 2006. U.S. Patent No 7,067,090. U.S. Patent and Trademark Office, Washington, DC.
- Hernandez, J.O., Choren, E.A., 1983. Thermal stability of some platinum complexes. *Thermochim. Acta* 71 (3), 265–272.
- Horiike, C., Morita, K., Okabe, T.H., 2012. Effective dissolution of platinum by using chloride salts in recovery process. *Metall. Mater. Trans. B* 43 (6), 1300–1307.
- Kalichini, M., Corin, K.C., O'Connor, C.T., Simukanga, S., 2017. The role of pulp potential and the sulphidization technique in the recovery of sulphide and oxide copper minerals from a complex ore. *J. South Afr. Inst. Min. Metall.* 117 (8), 803–810.
- Kraemer, D., Junge, M., Oberthür, T., Bau, M., 2015. Improving recoveries of platinum and palladium from oxidized Platinum-Group Element ores of the Great Dyke, Zimbabwe, using the biogenic siderophore Desferrioxamine B. *Hydrometallurgy* 152, 169–177.
- Landsberg, A., Schaller, J.L., 1971. The kinetics and equilibria of the platinum-chlorine system. *J. Less Common Met.* 23 (2), 195–202.
- Lee, J., Nagaraj, D., Coe, J., 1998. Practical aspects of oxide copper recovery with alkyl hydroxamates. *Miner. Eng.* 11 (10), 929–939.
- Lee, K., Archibald, D., McLean, J., Reuter, M., 2009. Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Miner. Eng.* 22 (4), 395–401.
- Lewins, J., Greenaway, T., 2004. The Pantan Platinum-palladium Project. The Australian Institute of Mining and Metallurgy Bulletin July-August 04.
- Li, Y., Kawashima, N., Li, J., Chandra, A.P., Gerson, A.R., 2013. A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. *Adv. Colloid Interface Sci.* 197–198, 1–32.
- Liddell, K.S., Adams, M.D., 2012. Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates. *J. South Afr. Inst. Min. Metall.* 112 (1), 31–36.
- Lottering, M.J., Lorenzen, L., Phala, N.S., Smit, J.T., Schalkwyk, G.A.C., 2008. Mineralogy and uranium leaching response of low grade South African ores. *Miner. Eng.* 21 (1), 16–22.
- Luszczkiewicz, A., Chmielewski, T., 2008. Acid treatment of copper sulfide middlings and rougher concentrates in the flotation circuit of carbonate ores. *Int. J. Miner. Process.* 88 (1), 45–52.
- Mahmoud, M.H., 2003. Leaching platinum-group metals in a sulfuric acid/chloride solution. *J. Min. Met. Mater. Soc.* 55 (4), 37–40.
- Malik, P., Paiva, A.P., 2010. A novel solvent extraction route for the mutual separation of platinum, palladium, and rhodium in hydrochloric acid media. *Solvent Extr. Ion Exch.* 28 (1), 49–72.
- Mpinga, C.N., Eksteen, J.J., Aldrich, C., Dyer, L., 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: a review. *Miner. Eng.* 78, 93–113.
- Mpinga, C.N., Eksteen, J.J., Aldrich, C., Dyer, L., 2017. Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore. *Miner. Eng.* 110, 153–165.
- Mpinga, C.N., Eksteen, J.J., 2018. Investigation into the flotation and direct leach performances of high-chromium PGM-bearing ore in oxidized mineralization. Unpublished under review.
- Mpinga, C.N., Eksteen, J.J., Aldrich, C., Dyer, L., 2018. A conceptual hybrid process flowsheet for platinum group metals (PGMs) recovery from a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization through a single-stage leach and adsorption onto ion exchange resin. *Hydrometallurgy* 178, 88–96.
- Muir, D.M., Ariti, J., 1991. Studies on the dissolution of platinum and palladium from low grade ores and by-products. In: 5th AusIMM Extractive Metallurgy Conference, Perth, Australia (2–4 Oct., 1991), pp. 183–186.
- Mwase, J.M., Petersen, J., 2017. Characterizing the leaching of sperrylite (PtAs₂) in cyanide based solutions. *Hydrometallurgy* 172, 1–10.
- Newell, A., Bradshaw, D., Harris, P., 2006. The effect of heavy oxidation upon flotation and potential remedies for Merensky type sulfides. *Miner. Eng.* 19 (6), 675–686.
- Nikoloski, A.N., Ang, K.L., 2014. Review of the application of ion exchange resins for the recovery of platinum-group metals from hydrochloric acid solutions. *Miner. Process. Extr. Metall. Rev.* 35 (6), 369–389.
- Oberthür, T., Melcher, F., Buchholz, P., Locmelis, M., 2013. The oxidized ores of the main sulphide zone, Great Dyke, Zimbabwe: turning resources into minable reserves-mineralogy is the key. *J. South Afr. Inst. Min. Metall.* 113 (3), 191–201.
- Okamoto, H., 1990. The As-Pt (Arsenic-Platinum) system. *J. Phase Equilibria* 11 (5), 508–510.
- Pospiech, B., 2012. Studies on platinum recovery from solutions after leaching of spent catalysts by solvent extraction. *Physicochem. Problems Min. Process.* 48 (1), 239.
- Renner, H., Schlamp, G., Kleinwächter, I., Drost, E., Lüscho, H.M., Tews, P., Panster, P., Diehl, M., Lang, J., Kreuzer, T., Knödler, A., 2001. Platinum Group Metals and Compounds. *Ullmann's Encyclopedia of Industrial Chemistry*.
- Robins, R.G., Jayaweera, L.D., 1992. Arsenic in gold processing. *Miner. Process. Extr. Metall. Rev.* 9 (1–4), 255–271.
- Schlecht, L., 1958. U.S. Patent No 2,829,967. Washington, DC: U.S. Patent and Trademark Office.
- Sefako, R., Sekgarametso, K., Sibanda, V., 2017. Potential processing routes for recovery of platinum group metals from Southern African oxidized PGM ores: a review. *J. Sustain. Metall.* 3 (4), 797–807.
- Shaik, K., Petersen, J., 2017. An investigation of the leaching of Pt and Pd from cooperite, sperrylite and column bioleached concentrates in thiocyanate-cyanide systems. *Hydrometallurgy* 173, 210–217.
- Sole, K.C., Feather, A.M., Cole, P.M., 2005. Solvent extraction in southern Africa: an update of some recent hydrometallurgical developments. *Hydrometallurgy* 78 (1), 52–78.
- Sun, P.P., Kim, T.Y., Min, B.J., Song, H.I., Cho, S.Y., 2015. Recovery of platinum from chloride leaching solutions of spent reforming catalysts by ion exchange. *Mater. Trans.* 56 (5), 738–742.
- Tatarnikov, A.V., Sokolskaya, I., Shneerson, Y.M., Lapin, A.Y., Goncharov, P.M., 2004. Treatment of platinum flotation products. *Platin. Met. Rev.* 48 (3), 125–132.
- Venkatesh, V., Pilchak, A.L., Allison, J.E., Ankem, S., Boyer, R.R., Christodoulou, J., Fraser, H.L., Imam, M.A., Kosaka, Y., Rack, H.J., Chatterjee, A., Woodfield, A., 2016. Proceedings of the 13th World Conference on Titanium. John Wiley & Sons.
- Yeates, R.C., Somorjai, G.A., 1983. The growth and alloy formation of copper on the platinum (111) and stepped (553) crystal surfaces; characterization by LEED, AES, and CO thermal desorption. *Surf. Sci.* 134 (3), 729–744.
- Zhou, S., Wei, Y., Li, B., Wang, H., Ma, B., Wang, C., 2016. Mechanism of sodium chloride in promoting reduction of high-magnesium low-nickel oxide ore. *Sci. Rep.* 6.

CHAPTER V : PRACTICAL APPROACH TO PGMs RECOVERY FROM ORES IN OXIDIZED MINERALIZATION AND SUBSEQUENT LEACHATES

Submitted for publication as

A conceptual hybrid process flowsheet for platinum group metals (PGMs) recovery from a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization through a single-stage leach and adsorption onto ion exchange resin.

Cleoplace Ngoie Mpinga, Jacques Eksteen, Chris Aldrich, Laurence Dyer., 2018.
Hydrometallurgy 178, 88-96.

Accepted for publication on 31st March 2018.

© 2018 Elsevier Ltd.

Reprinted with permission from the publisher.

SUMMARY

The Chapter examined under laboratory batch-scale conditions, the technical feasibility of using commercially available anion exchanger diethylaminoethyl cellulose (DEAE) for the separation and preconcentration of Pt(IV) and Pd(II). The emergent findings of the investigation are presented. A conceptual flowsheet is disclosed for hydrometallurgical pilot scale testing, economic evaluation and assessment of potential environmental impacts.



A conceptual hybrid process flowsheet for platinum group metals (PGMs) recovery from a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization through a single-stage leach and adsorption onto ion exchange resin

Cleoplace Ngoie Mpinga, Jacobus Johannes Eksteen*, Chris Aldrich, Laurence Dyer

Western Australian School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, GPO Box U1987, Perth 6845, Western Australia, Australia

ARTICLE INFO

Keywords:

Oxidized mineralization
Chloride PGM-bearing solutions
Competitive adsorption
Commercially available DEAE anion exchange resin
Thiocyanate addition
Adsorption isotherms

ABSTRACT

The availability of oxidized PGM ore deposits, at or near the earth's surface, present lucrative prospects for future PGM production owing to the large resource estimates, the relatively high PGM grades and they can be mined through relatively lower-cost open-pit mining processes. However, these oxidized PGM ores are currently not mined or treated due to insufficient recoveries using established metallurgical techniques. The complex mineralogy and polymodal distribution of PGM in the oxidized ores pose a number of challenges to the metallurgist from a mineral liberation and extraction perspective.

A conceptual route to the integrated processing of a Ni-Cu-PGM bearing chromite ore in oxidized mineralization for the recovery of base and precious metals is presented based upon earlier work of the authors and recent research on metal recovery from solution. This paper presents laboratory batch-scale results of simultaneous adsorption of Pd(II) and Pt(IV) onto commercially available weak-base anion exchange resin, diethylaminoethyl (DEAE) cellulose, from hydrochloric acid solutions. Effects of various variables such as equilibration time, thiocyanate and tin chloride concentrations were studied.

Without any prior scrubbing step to remove co-extracted impurities, the uptake of Pd(II) and Pt(IV) was successfully accomplished with recoveries approximating 100% within 15 min. The presence of Fe(III) and other non-ferrous metal accompanying ions didn't show any marked tendency to adsorb. Among the adsorption parameters, thiocyanate concentration had the most significant effect on the process. The dual role of Sn(II) i.e. labilizing agent and PGM collector at a time, was simply overridden, overshadowed by the DEAE high selectivity for PGMs. Thiourea proved to be a better stripping reagent for bulk elution of combined Pd(II) and Pt(IV). A conceptual flowsheet is disclosed for hydrometallurgical pilot scale testing, economic evaluation and assessment of potential environmental impacts.

1. Introduction

The availability of oxidized platinum group metal (PGM) ore deposits, at or near the earth's surface, present lucrative prospects for future PGM production owing to the large resource estimates, the relatively high PGM grades and they can be mined through relatively lower-cost open-pit mining processes (Oberthür et al., 2013; Evans, 2002).

However, these oxidized PGM ores are currently not mined or treated due to insufficient recoveries using established metallurgical techniques (Kraemer et al., 2015; Becker et al., 2014; Bulatovic, 2003). The complex mineralogy and polymodal distribution of PGMs in the oxidized ores pose a number of challenges to the metallurgist from a

mineral liberation and extraction perspective (Kraemer et al., 2017; Cabri et al., 2017).

A process approach has been developed and evaluated for treating PGM-bearing chromite ores in oxidized mineralization (with platinum content predominantly mineralized as sperrylite, and palladium as palladium antimonides) at atmospheric pressure in order to recover metal values contained therein (Mpinga et al., 2017b). Single-stage molten salts chlorination roast-leach process was the treatment scenario observed for leaching simultaneously said metal values without the need and/or addition of oxidizing agents.

Using cheap and readily available reagents — CaCl₂ and MgCl₂ are routinely used for snow and ice control on roadways — the process

* Corresponding author.

E-mail address: jacques.eksteen@curtin.edu.au (J.J. Eksteen).

<https://doi.org/10.1016/j.hydromet.2018.03.024>

Received 14 January 2018; Received in revised form 11 March 2018; Accepted 31 March 2018

Available online 10 April 2018

0304-386X/ © 2018 Elsevier B.V. All rights reserved.

Nomenclature		n	Freundlich exponent, it measures the deviation from linearity
B	Langmuir constant that relates to the affinity of binding sites, L/mg	q_e	Loading of a metal on the resin at equilibrium, mg/g
C_0	Initial concentration of ions in the solution, mg/L	Q_m	Theoretical saturation adsorption capacity of the monolayer, mg/g
C_e	Equilibrium concentration of ions in the solution, mg/L	q_t	Adsorption capacity of the resin at time t , mg/g
k_f	Freundlich constant related to adsorption capacity of adsorbent, $(\text{mg/g})/(\text{mg/L})^{1/n}$	R_L	Dimensionless separation constant

typically entailed the mixing of run-of-mine ore with abovementioned chlorinating salts on weight percent basis ratio of 1:3 (with equal weight ratio of CaCl_2 and MgCl_2) in a porcelain crucible which resulted in a sticky paste-like material.

The charged and covered material was placed in an unvented electric or static air roast muffle furnace equipped with a programmable temperature controller, and was gradually heated under normal atmospheric pressure and oxygen partial pressure conditions at 650 °C for 6 h residence time.

Afterwards the roast calcine was leached in 6 M HCl, that mimicks typical industrial concentration, at 90 °C for 24 h. Excellent leach beneficiation averaging 99.71% Pt and 100% Pd was recorded, with relatively low co-extraction of deleterious chromium (0.31%). Therefore, high Cr content can be allowed in the flotation concentrate without adversely affecting PGM recovery.

Although PGM solubilisation was an important measure of the overall success of the processing method, the degree to which these are recovered from pregnant solutions was equally important. PGM chloro-complexes are generally recovered from pregnant solutions by using the classical process, which basically involves successive series of salts precipitation and redissolution steps, and a final thermal reduction to metal (Demopoulos, 1989). Nevertheless, such method is considered inefficient by today's standards in terms of the degree of separation achieved, the yields obtained and the complexity of operations involved (Gaita and Al-Bazi, 1995; Demopoulos, 1989).

The classical method is also not satisfactory for recovering desired element(s) from diluted media containing precious metals in trace amounts (Waitz Jr, 1982). Thereby, the introduction of new methods for meeting such rising analytical standards has been important to the platinum industry. In this regard, solvent extraction and ion exchange have been introduced and adopted by some precious metal refineries (Nikoloski et al., 2015; Demopoulos, 1989).

The objective of the present work was to examine under laboratory batch-scale conditions, the technical feasibility of using commercially available anion exchanger diethylaminoethyl cellulose (DEAE) for the separation and preconcentration of Pt(IV) and Pd(II) in aqueous HCl. The process could be accomplished by two different routes: (1) selective extraction of each metal or, (2) group extraction followed by selective stripping. The latter option was adopted for this study, but with a single bulk strip of PGMs. This paper presents and discusses the recovery test results.

2. Theoretical background

2.1. Classical technique for recovering PGMs from pregnant solutions

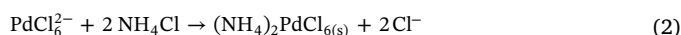
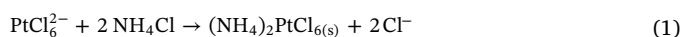
Until the 1970s, PGM recovery and separation in precious metal refineries had been achieved by a series of precipitation processes

Table 1
Physicochemical properties of anion exchange resin DEAE cellulose.

Trade name	Functional group	Exchanger type	Matrix	^a Operating pH range	Capacity (meq/g)	Bead size range (μm)
DEAE cellulose	Diethylaminoethyl	Weak-base	Cellulose	2 to 9.5	1 to 1.5	20 to 60

^a DEAE has been used in 2 M HCl by Al-Bazi and Chow (1984).

exploiting differences in the chemistry of their anionic chloro-complexes (Nikoloski et al., 2015; Koch et al., 2006; Bernardis et al., 2005). Platinum in its tetravalent oxidation state is selectively precipitated as diammonium hexachloroplatinate(IV), $(\text{NH}_4)_2\text{PtCl}_6$, by saturating the mother liquor with ammonium chloride (Eq. (1)); whereas after oxidation to palladium(IV), this latter ion is similarly precipitated (Eq. (2)) as diammonium hexachloropalladate(IV), $(\text{NH}_4)_2\text{PdCl}_6$ (Gaita and Al-Bazi, 1995).



The complexity of this classical technology, sometimes referred to as a 1st generation process, proved to have poor selectivity toward PGMs. Currently, the majority of platinum producing companies make use of newer technologies to refine PGMs by 2nd generation (solvent extraction) and 3rd generation (ion exchange and/or molecular recognition) processes (Nikoloski and Ang, 2014; Crundwell et al., 2011; Demopoulos, 1989). These last two generations are recognised as potentially more efficient and economically justified, even for solutions containing very low PGM concentrations (Nikoloski et al., 2015).

2.2. Ion exchange resin (IX) as alternative approach for PGMs recovery

2.2.1. Choice of ion exchangers

PGM chloro-complexes have an extremely high affinity for strong-base resins. This affinity is so high that quantitative elution is difficult and their recovery from the loaded resins is completed by combustion (Kononova et al., 2014; Shams and Goodarzi, 2006; Kyriakakis, 2005; Demopoulos, 1989). The burning practice is considered economical, owing to both high PGM loading on the resin and their high values.

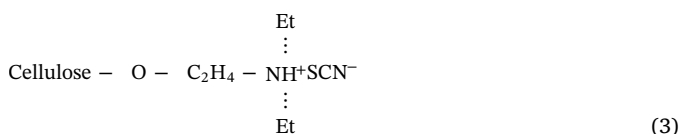
Despite the abovementioned high affinity, strong-base resins have not found significant commercial application in PGM circuits, other than being metal scavengers from dilute streams (Kyriakakis, 2005). The problem with these exchangers is that commercially available resins do not selectively adsorb negatively charged Pt(IV) and Pd(II) chloro-complexes (Godlewska-żykiewicz, 2004). In other words, they are not highly selective against iron, the common major solution impurity.

2.2.2. Weak-base anion exchanger diethylaminoethyl (DEAE) cellulose

As far as could be determined, the earlier work reporting on selective adsorption of PGM ions from mixed thiocyanato-chloride media is a series of papers by Kuroda et al. (1968), who used the weak-base anion exchange DEAE cellulose in Table 1.

Kuroda et al. (1968) demonstrated the possibility of separating and concentrating PGM ions from a large quantity of base metals, such as iron, cobalt, nickel, copper, zinc and lead in a small column of DEAE in

its thiocyanate form as depicted in Eq. (3); where Et refers to Ethyl group: $-\text{CH}_2\text{CH}_3$ (Kaminski Jr, 1970). The primary adsorption mechanism is an anion exchange that occurs via the tertiary amine functional group. Anionic species are adsorbed through displacement of an associated counter ion (Smith and Moody, 1991).



Furthermore, noble metal ions adsorbed were easily stripped from DEAE using either only one eluant — isocratic elution which simplifies the process — or a mixture of reagents as shown in Table 2.

Table 2
DEAE ion exchange adsorption and elution of Pd(II) and Pt(IV).

Metals adsorbed	Medium	Eluent(s)	Reference
Pd(II)-Pt(IV)	0.02 M NH_4SCN 2 M HCl	Pt: a mixture of 0.02 M NH_4SCN and 2 M HCl Pd: 0.05 M thiourea	Al-bazi and Chow (1984)
Pd(II)-Pt(IV)	1 M HCl 0.01 M SCN^-	0.05 M thiourea $\text{SC}(\text{NH}_2)_2$ or a mixture of 4 M HCl and 2 M HClO_4	Ishida et al. (1968)

2.2.3. Adsorption prerequisites: HCl and SCN^- concentrations

Warszawsky (1983) reported that the adsorption of chloride complexes of transition metals ions, including PGM ions, onto anion exchange resins was acid dependent. Platinum, palladium and gold adsorption was high from dilute HCl solutions titrating 0.01 to 0.5 M, whereas the adsorption of Rh, Ir, Ru, Os and other transition metals (particularly Fe, Ni, Cu and Co), increased with increasing HCl concentration.

In chloride media containing low concentrations of thiocyanate ions, Ishida et al. (1968) noticed at pH values of 1 to 3, that the chloride form of DEAE substantially lowers K_d values for Pt(IV) and Pd(II), as compared with values found for DEAE in the thiocyanate form. This suggests that for efficient Pd(II) and Pt(IV) extraction, DEAE in the thiocyanate form is decidedly preferable to its chloride form, especially when the concentration of chloride in solution is high.

2.2.4. Kinetics of adsorption — effect of test interruptions on PGMs adsorption rate — rate-determining step

Generally typical liquid/solid adsorption involves film diffusion, intraparticle diffusion and mass action. Two trends are usually used to evaluate adsorption kinetics. These are (1) adsorption reaction models, e.g. pseudo-first-order, pseudo-second-order kinetic equations and the Elovich model and, (2) adsorption diffusion models, including intraparticle diffusion model and liquid film diffusion model.

To this end, Zolgharnein and Shahmoradi (2010) emphasized that one of the following phenomena can be the rate-determining step of an adsorption process: (1) diffusion through the boundary layer to the surface of the adsorbent (external diffusion), (2) adsorption of ions onto sites, and (3) intraparticle diffusion into the interior of the adsorbent. For physical adsorption, mass action is a rapid process and can be negligible for kinetic studies. Thus, the kinetic process of adsorption is always controlled by liquid film diffusion or intraparticle diffusion, i.e. one of the processes should be the rate limiting step.

Kumar and Jain (2013), Zipperian and Raghavan (1985), and Fleming and Cromberge (1984) used interrupted batch adsorption tests to demonstrate the importance of both film diffusion and intraparticle mass transfer. If a process is controlled by particle diffusion, the rate of

extraction immediately after the interruption should be faster (following the re-immersion) than it was before the interruption (Fleming and Nicol, 1984). Otherwise the process is film diffusion controlled.

2.2.5. Equilibrium data and adsorption modeling

The empirical Freundlich and Langmuir models are among isotherms generally used to describe single solute adsorption equilibrium onto either activated carbon or ion exchange resins and to investigate its mechanism (Nikoloski et al., 2015; Crundwell, 2013; Zhou et al., 2009). Note that these two isotherms are not predictive, since variables such as the solution pH and the ionic strength change with changing conditions (Pesavento et al., 2010).

2.2.5.1. Empirical Freundlich isotherm. The Freundlich isotherm (Eq. (4)) is derived theoretically under the assumption that the adsorption energy obeys an exponential distribution. It describes the multilayer formation of adsorbate on the heterogeneous solid surface of the adsorbent. The model assumes heterogeneous adsorption due to the diversity of adsorption sites or diverse nature of metal ions adsorbed, free or hydrolysed species. The assumptions in this model are also that stronger binding sites are occupied first and that the binding strength decreases exponentially with the increasing degree of site occupation (Nikoloski and Ang, 2014; Adams et al., 1987).

$$q_e = k_f C_e^n \quad (4)$$

k_f and n are Freundlich parameters representing the adsorption capacity and the intensity (surface heterogeneity), respectively. The Freundlich exponent “ n ” measures the adsorption deviation from linearity. If $n = 1$, then the adsorption is linear; if $n < 1$, the adsorption is a chemical process; if $n > 1$, then adsorption is a physical process (SenthilKumar et al., 2012). Higher k_f values indicate higher affinity for a given species. k_f and n can be determined from the intercept and slope of the linear plot of $\log(q_e)$ vs. $\log(C_e)$ (Eq. (5)). However, the Freundlich model does not provide information such as maximum loading as the Langmuir isotherm does.

$$\log q_e = \log k_f + n \log C_e \quad (5)$$

where $\log k_f =$ y-intercept and $n =$ slope.

2.2.5.2. The Langmuir isotherm. The Langmuir isotherm in Eq. (6) is based on the following assumptions: (1) the adsorption energy of all sites is the same (constant), and is unaffected by the adsorption on neighbouring sites; (2) the adsorption is immobile; (3) each site accommodates only one adsorbed particle (monolayer adsorption); and (4) adsorbed atoms (molecules) do not interact with each other (Paunovic and Schlesinger, 2006). This isotherm model reduces to a linear form at low concentrations.

$$q_e = \frac{Q_m B C_e}{1 + B C_e} \quad (6)$$

Solving the Langmuir Eq. (6) gives linearized Eq. (7).

$$\frac{1}{q_e} = \left(\frac{1}{B Q_m} \right) \left(\frac{1}{C_e} \right) + \left(\frac{1}{Q_m} \right) \quad (7)$$

Therefore, a plot of $1/q_e$ versus $1/C_e$ gives a straight line of slope $(1/BQ_m)$ and intercept $(1/Q_m)$. A large parametric B value indicates high selectivity of the resin for a particular metal ion species.

$$R_L = \frac{1}{1 + B C_0} \quad (8)$$

The dimensionless separation constant or equilibrium parameter R_L (Eq. (8)) can be used to express whether an adsorption system is favourable or unfavourable. It is irreversible for $R_L = 0$, favourable if $0 < R_L < 1$, linear for $R_L = 1$ or unfavourable if $R_L > 1$. According to Dabrowski (2001), the Langmuir isotherm is applicable to chemisorption and with some restrictions to physisorption. Therefore in this

investigation, an adequate isotherm will be suggested based on Fisher z-transform expressed in Eq. (9)). Note that Fisher z-transform normalizes the distribution of the correlation coefficients, allowing average correlations and standard deviations to be calculated more accurately (Gorsuch and Lehmann, 2010).

$$z = 0.5 \ln\left(\frac{1+r}{1-r}\right) \quad (9)$$

where r denotes correlation coefficient.

3. Materials and methods

3.1. Materials

3.1.1. Stock solutions

Owing to insufficient quantity of material to produce enough leach liquor, ion exchange tests have been conducted on synthetic solutions that almost mimicked expected typical industrial leach liquors. The leachate generated in Mpinga et al. (2017b)'s experimental program at solid-to-liquid ratio of 5%w/v in 6 M HCl served in part for the preparation of such synthetic solutions. However, the expectation for ideally using low-grade rougher concentrates at high flotation mass pull (e.g. 10%) will more likely increase PGMs concentration in the leachates.

Synthetic stock solutions of major species were prepared by dissolving appropriate amount of chloride salts of analytical grade in 2.5 M HCl, which was the average residual acid concentration in the process pregnant leachates. For abovementioned reasons, it seemed more reasonable to suggest synthetic solutions (Table 3) containing approximately 8 times the amount of Pt and 7 times that of Pd present in the process leachates (Mpinga et al., 2017b). Changes of these conditions will be specified in saturation loading capacity tests. Suitable amounts of SCN(I) and Sn(II) were afterward added to the stock solutions to start the adsorption process.

3.1.2. Adsorbent pretreatment

The anion exchange resin diethylaminoethyl (C₂₀H₂₃O₅) from Toronto Research Chemicals was obtained in the form of 20 to 60 μm insoluble white beads with approximately 70% moisture content. Before its use, a known amount was soaked in 1 M NaSCN for 24 h to convert it into thiocyanate form. The resin was then thorough rinsed with deionized water until the rinsing water pH was approximately neutral. The prepared resin was then stored in sealed flasks, with deionized water added to keep it hydrated, ready to be used for isotherm and kinetic tests. DEAE in the chloride form was also used.

3.2. Methods

3.2.1. Adsorption stage

Batchwise adsorption tests were performed in open-ended rolling bottles to allow free circulation of oxygen. These were rotated at 105 rpm as this was the maximum speed of the device used. Although Ishida et al. (1968) reached the equilibrium within 15 h at 25 °C when using similar adsorbent for Pt(IV) and Pd(II) adsorption, in this study the mixture (resin and solution) was rotated for 24 h to ensure that the equilibrium was attained. Individual levels of the two selected adsorption input factors (taken from Mpinga et al., 2017b) are shown in Table 4.

Simulating multi-stage countercurrent loading operations, 5 g of resin was contacted with 500 mL of solution and allowed to equilibrate at

Table 3

Averaged amount of base and precious metals in mixed synthetic solutions.

Species	Pt(IV)	Pd(II)	Co(II)	Cr(III)	Cu(I)	Ni(II)	Fe(III)	Mg(II)	Ca(II)
mg/L	5	5	50	100	1000	1000	5000	10,000	20,000

Table 4

Individual levels of the two operating factors.

Operating factors	Levels	
	Low	High
SCN(I) concentration (M, g/L)	0	0.01 (0.58)
Sn(II) concentration (M, g/L)	0	0.001 (0.12)

room temperature for 24 h. After filtration, the partially loaded resin was then placed into another 500 mL of fresh pregnant solution for the same length of time, after which the separation process was again conducted. The procedure, also called “repeating contact technique”, was continued for a couple of cycles to produce isotherms covering the full range of metal ion concentrations in solution and on the resin that would be found in typical counter-current applications (Fleming and Cromberge, 1984).

Samples were collected before and after each contact. The initial and final solution concentrations of metal ions present in the solution were then plotted together to generate equilibrium isotherms as illustrated in Fig. 2. Loading on the resin was determined by mass balance over each contact, and a cumulative loading over the cycles could also be calculated.

3.2.2. Elution stage

The desorption of adsorbed metal ions was studied under dynamic conditions in a fixed-bed glass column with ~9 mm interior diameter and ~45 cm height. The exchange column previously filled with distilled water was then filled with the loaded resin until it settles. This procedure was imperative as it prevents air spaces (bubbles) in the resin bed which would lead to channelling. Acting as a calming zone, glass beads were added to improve the flow distribution avoiding physical disturbance of the resin bed. The loaded resin was eluted for PGMs using various fresh bed volumes of 0.05 M thiourea (Ishida et al., 1968).

It should be noted that a bed volume relates to the volume (25 mL in this investigation) of the empty column (Davidson and Schmidt, 1986). The eluent was downward passed through the column at the flow rate of 1 mL/min controlled by a peristaltic pump (Fontàs et al., 2009; Gaita and Al-Bazi, 1995; Ishida et al., 1968). In this context, Weber (1997) stated that ion exchange process cannot occur efficiently if the flow rate is too high. In both adsorption and elution studies, aliquot samples of 2 mL were collected at predetermined time intervals or at specific bed volume intervals and analyzed for residual metals by means of ICP-MS.

4. Results and discussion

4.1. Effect of equilibration time on Pd(II) and Pt(IV) adsorption rate

As it is an important variable in validating the adsorbent choice, time progression was examined to ensure optimal and quantitative real-time uptake of targeted metal ions. The adsorption percentage vs. time plotted in Fig. 1 demonstrates that both Pd(II) and Pt(IV) adsorption were fast and equilibrium was reached within the first 30 min achieving 100% as compared to base metals, such as Cu, Cr and Fe, which needed extended adsorption time up to 24 h to reach ~8%, with the shape of their curves indicating that plateaus have been reached. This is consistent with findings by Ishida et al. (1968), who successfully separated trace amounts of Pt(IV) and Pd(II) from large quantities of common base metal ions at 25 °C.

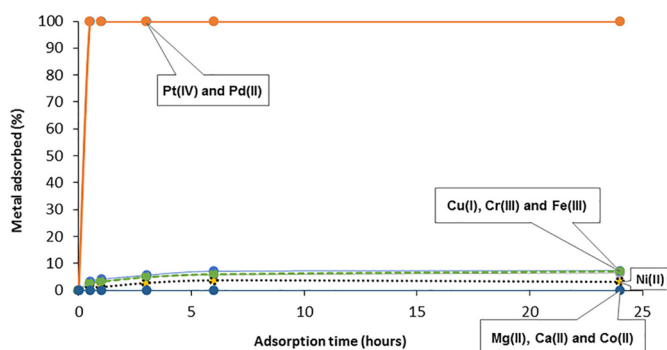


Fig. 1. Comparative curves showing adsorption kinetics of PGMs and selected common accompanying ions in synthetic chloride solutions using DEAE cellulose resin at solid-to-liquid ratio of 1%w/v and room temperature. Feed solution: 0.58 g/L SCN(I), 0 g/L Sn(II), 5 mg/L Pt(IV), 5 mg/L Pd(II), 50 mg/L Co(II), 100 mg/L Cr(III), 1 g/L Cu(I), 1 g/L Ni(II), 5 g/L Fe(III), 10 g/L Mg(II) and 20 g/L Ca(II) contained in 2.5 M HCl.

Table 5

Experimental layout and results for the 15 min adsorption tests.

Trial	Factors (g/L)		Precious and base metals adsorbed (%)						
	SCN(I)	Sn(II)	Pt(IV)	Pd(II)	Cu(I)	Ni(II)	Fe(III)	Cr(III)	Co(II)
1	0.58	0	100	100	0.16	0	0.20	0.34	0
2	0.58	0.12	100	100	0	0.06	0.14	0.04	0.16
3 ^a	0.58	0.12	100	100	0	0.01	0	0	0.12
4	0	0.12	65.40	99.98	0.97	2.45	1.21	2.80	0.22
5	0	0	67.05	99.95	0	0	0	0	0
6 ^a	0	0	36.08	32.22	0	0.86	0	0	0.33

^a Denotes resin used as received without prior thiocyanate soaking pretreatment.

Attempts have been made to address base metal co-adsorption, i.e. by shortening the adsorption time (Table 5). In general, the presence of Fe(III) and other accompanying non-ferrous metal ions do not show any marked tendency to adsorb. It is likely that their actual co-adsorption is ascribed to decreased concentrations of Pt(IV) and Pd(II) that creates a large concentration gradient, which determines the driving force of the overall uptake rate.

However, these co-adsorbed metals can be displaced with appropriate wash solutions. In this context, prior to elution, Ishida et al. (1968) scrubbed the loaded DEAE resin with a mixture of 0.01 M NH_4SCN and 0.1 to 1 M HCl to remove co-extracted base metal impurities. Platinum and palladium were then stripped with 0.05 M $\text{SC}(\text{NH}_2)_2$.

4.2. Effect of SCN^- and Sn^{2+} initial concentrations on Pd(II) and Pt(IV) adsorption rate

The experimental layout and results of the 15 min adsorption trials are listed in Table 5. The effect of thiocyanate concentration on PGMs adsorption rate was examined in the 0 to 0.01 M (0.58 g/L) range. The results indicate a rapid increase in platinum extraction from 67.05% at zero SCN(I) concentration to a maximum of 100% at 0.58 M SCN(I), with which 99.95% of the palladium was extracted (Tests 1, 5 and/or 4).

In addition, the results indicate that the presoaking of the resin (converting its sites with desired SCN^- counter ions) has huge effect on the adsorption mechanism only in complete absence of SCN(I) in solution (Tests 3 and 6). Irrespective of Sn(II) composition in the leach liquor, tests with virgin and presoaked resins gave 100% adsorption of both Pt(IV) and Pd(II) in presence of SCN(I) (Tests 1, 2 and 3). Note that the increased amount of calcium and magnesium in solution didn't cause any solution scaling.

The effect of Sn^{2+} concentration on PGM adsorption rates was examined in the 0 to 0.001 M (0.12 g/L) range. At zero Sn(II), 100% Pt

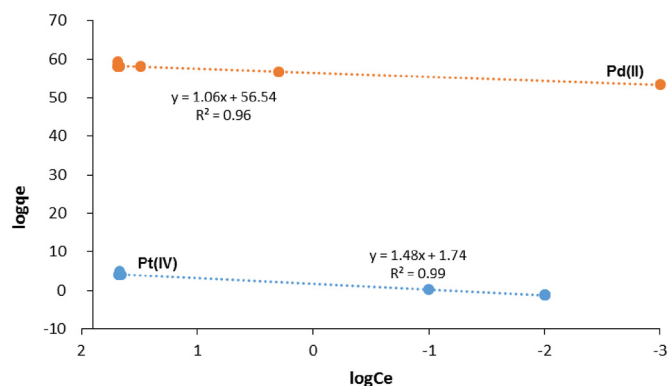


Fig. 2. Equilibrium adsorption isotherms for Pt(IV) and Pd(II) loading onto 10 g/L anion exchanger DEAE cellulose for 15 min contact time at room temperature. Feed solution: 0.58 g/L SCN(I), 0 g/L Sn(II), 50 mg/L Pt(IV), 50 mg/L Pd(II), 50 mg/L Co(II), 1 g/L Cu(I), 1 g/L Ni(II), 5 g/L Fe(III), 10 g/L Mg(II) and 20 g/L Ca(II) contained in 2.5 M HCl.

(IV) and 100% Pd(II) were extracted (Test 1). Hence the effect of Sn(II) concentration was not as important as the effect of SCN(I) concentration in determining the most appropriate processing route.

Adsorption tests in the presence and/or absence of Sn(II) at a time as a collector and a stabilizing agent — but in presence of SCN(I) — gave approximately similar PGM recoveries of 100% (Tests 1, 2 and 3). It can be inferred that its dual role was simply overridden, overshadowed by the high selectivity of DEAE for PGMs. Hence SCN(I) initial concentration was the most important variable for the overall adsorption of the two adsorbates.

4.3. Evaluation of adsorption isotherm models

The adsorption data were fitted with both Langmuir and Freundlich isotherm models. Based on the Fisher z-transform (See Appendix A) of correlation coefficient values obtained from the data in Fig. 2, the Freundlich model provided a better fit than the Langmuir model in the case of Pt(IV), but not so with Pd(II) at a 95% confidence level.

4.4. Adsorption rate controlling step

During the loading sequences, partially loaded resins were separated from solutions for 2 h per cycle. From the interruption test results given in Fig. 3, an increase can be seen in kinetics taking place after every resin re-immersion in solutions. This means that intraparticle diffusion was the prominent mechanism in operation as the rate controlling step. In other words, interruption tests strongly indicated that film diffusion was minimal or non-existent.

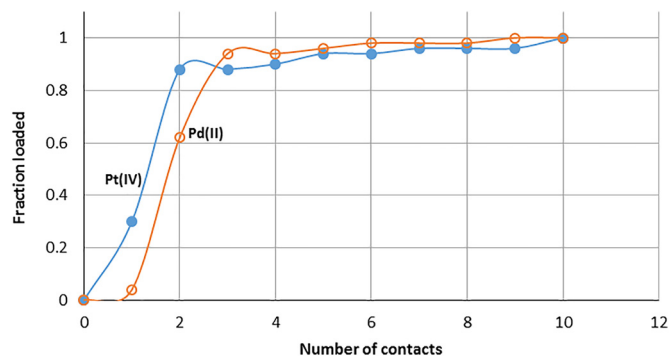


Fig. 3. Effect of interruption tests on Pd(II) and Pt(IV) adsorption rate onto DEAE cellulose. Feed solution: 0.58 g/L SCN(I), 0 g/L Sn(II), 50 mg/L Pt(IV), 50 mg/L Pd(II), 50 mg/L Co(II), 1 g/L Cu(I), 1 g/L Ni(II), 5 g/L Fe(III), 10 g/L Mg(II) and 20 g/L Ca(II) contained in 2.5 M HCl.

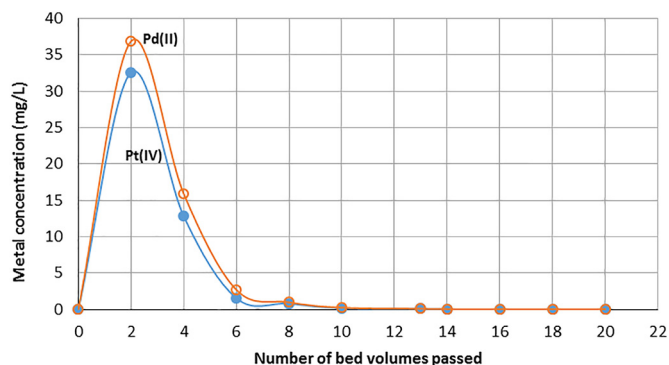
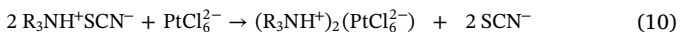


Fig. 4. Isocratic elution profile of metal ions from loaded DEAE cellulose resin containing 32.57 and 36.86 mg/g of Pt and Pd respectively using 0.05 M thiourea SC(NH₂)₂ as eluant at flow rate of 1 mL/min (2.4 bed volumes per hour) and room temperature.

It is clear that Pt(IV) and Pd(II) were extracted into the resin up to 7th contact, and thereafter remained almost constant. The cumulative loading capacity of DEAE cellulose for these two metals was observed to be respectively 32.57 and 36.86 mg/g representing 90.69% of the overall loading capacity. A higher loading capacity implies better utilization of the resin. In addition, high adsorption capacity avoids excess resin to elution stage. The adsorption mechanism of PGMs involves the fixation of their chloro-anion complexes on the positively charged amino group in a “purely” anion exchange extraction mechanism as illustrated in Eq. (10).



Where R₃NH⁺SCN⁻ denotes anion exchanger diethylaminoethyl cellulose in its thiocyanate form.

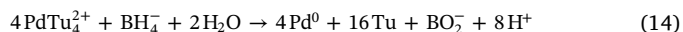
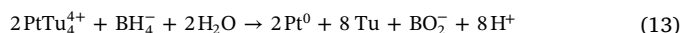
4.5. Isocratic elution process of Pd(II) and Pt(IV) from loaded resin matrix

Elution curves for bulk stripping of combined Pd(II) and Pt(IV) are shown in Fig. 4. More than 99% of both palladium and platinum was

successfully eluted in only two bed volumes (1 bed volume = 25 mL) under ambient conditions, resulting in a small volume of highly concentrated PGMs eluate which is suitable for downstream processing. Note that a comprehensive discussion on elution process is beyond the intended scope of this research, however according to Dyosi et al. (2009), the elution reactions might be explained by Eqs. 11 and 12. For reasons of convenience and presentation “Tu” denotes SC(NH₂)₂ i.e. thiourea molecule.



PGMs are then recovered from thiourea strip liquors by reduction-precipitation using alkali metal borohydride e.g. NaBH₄, according to reactions in Eqs. (13) and (14). Awadalla et al. (1994) stated that PGMs reduction by NaBH₄ increases with temperature increase and is fast i.e., the reaction is complete within 1 min and reduced products are stable for at least 12 h.



4.6. Conceptual flowsheet

Based on above experimental results and observations, and earlier research relating to the salt-baking and leaching of the PGM-bearing chromitite ore in oxidized mineralization, a conceptual flowsheet for recovering principal pay metals i.e., Cu, Ni, Pd and Pt, is proposed for hydrometallurgical pilot scale testing, economic evaluation and assessment of potential environmental impacts. Its recovery unit operations include, among others, the molten salt chlorination roast and the standard ion exchange resin technology, which plays pivotal roles in the schematic flow diagram displayed in Fig. 5.

This is a radical redesign of the process developed for the Pantom deposit in Western Australia (Fig. 6) with the aim of reducing its reagents consumption, downtime and the avoidance of its major drawback of burning the resin in order to recover the loaded precious metals.

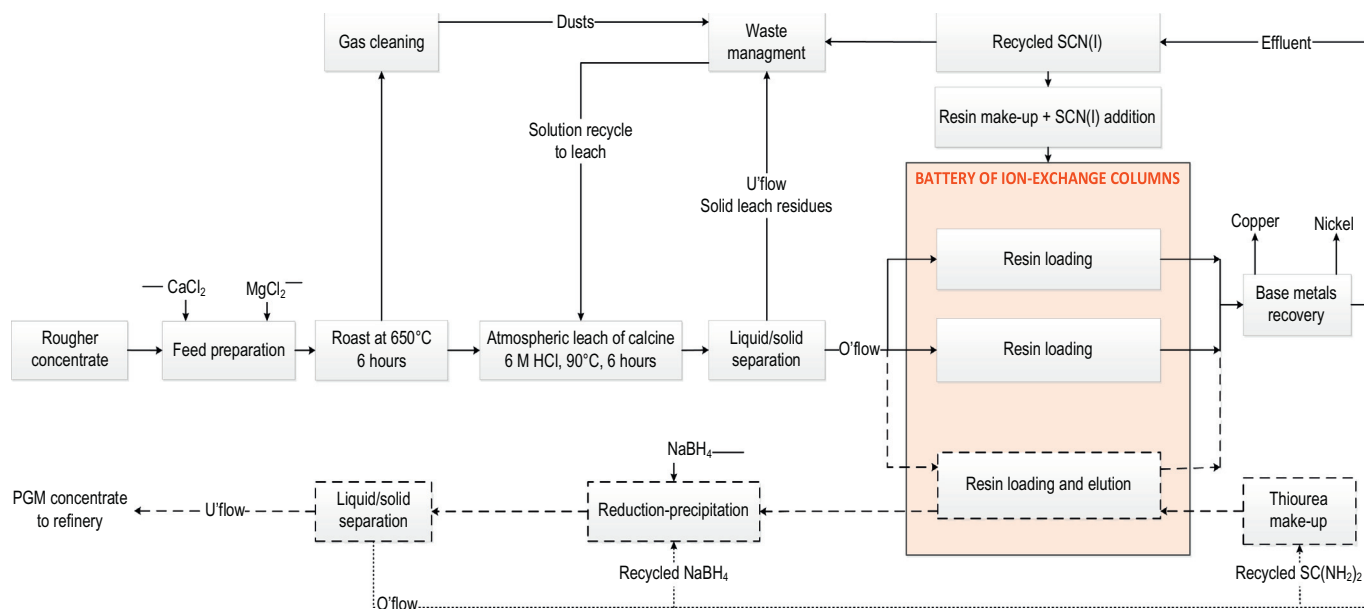


Fig. 5. Conceptual hybrid process flowsheet for platinum group metals (PGMs) recovery from a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization through a single-stage leach and adsorption onto ion exchange resin. Dashed lines indicate the switching to elution and regeneration mode when the resin in a column is fully loaded with precious metals.

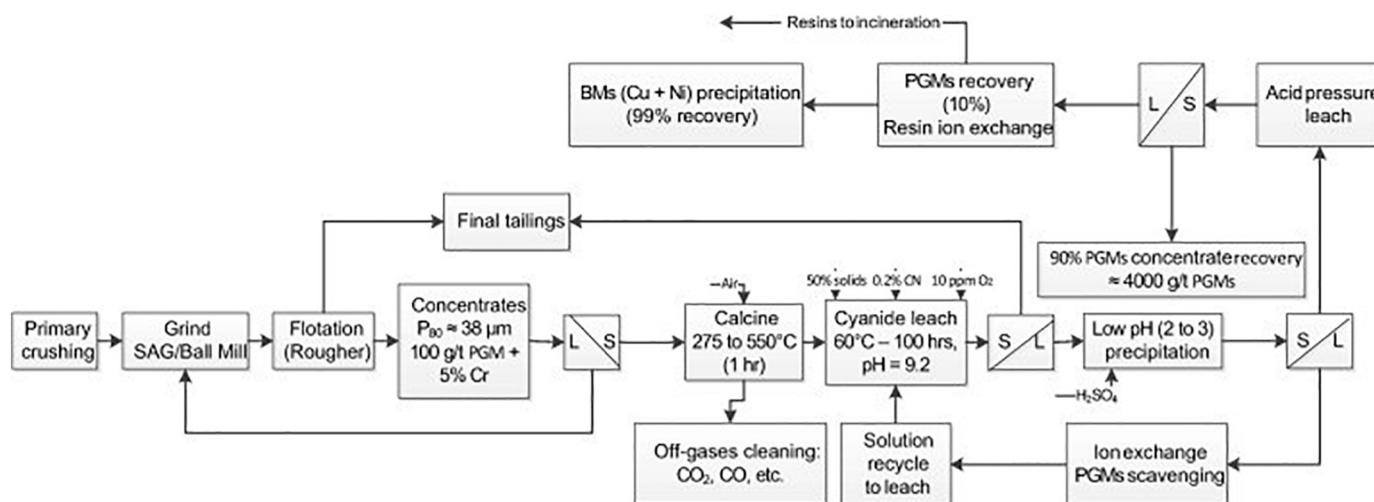


Fig. 6. Panton process conceptual flow schematic (Lewins and Greenaway, 2004).

Resin regeneration is crucially important for keeping the process cost down. Of special interest is the non-requirement of a swing in solution pH that would not only incur higher operating costs for additional reagent make-up downstream, but also the potential of releasing HCN due to cross contamination.

The original “Panton process” was developed for the high-chromite Panton Sill ore in oxidized mineralization which was problematic as the deposit size and remoteness could not justify the erection of a smelter, and the high chromite content of the flotation concentrates made it difficult to secure an offtake agreement with existing smelters at the time (2003–2007). Additional information on flowsheet complexity and shortcomings of the “Panton process” is found in Mpinga et al. (2017a).

The solubilisation of PGMs was the prime driving force behind the flowsheet (Fig. 5) development and optimization. Their dissolution rate is high enough to be considered for scale-up (Mpinga et al., 2017b). Owing to its high selectivity for PGMs, DEAE resin can be scaled down in small columns, on which trace concentrations of PGMs can be retained from very large volumes of base metals and other common accompanying ions. In order to minimize resin handling and associated resin losses, adsorption and elution may be performed in a same column. In practice, according to McKeivitt (2007), automatically switching the column from loading to stripping after a designated number of bed volumes could easily be achieved by programming a process logic controller (PLC).

5. Conclusions

In another laboratory evaluation, the hybrid pyro-hydro-metallurgical and low-temperature single-stage molten salt (CaCl₂/MgCl₂) chlorination technique proved successful for simultaneously and efficiently enable leaching a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization without the need and/or addition of further oxidizing agents. Excellent leach beneficiation was achieved averaging 99.71% Pt and 100% Pd with relatively low co-extraction of deleterious

chromium (0.31%). Therefore, high Cr content can be allowed in the flotation concentrate without adversely affecting PGM recovery.

Using weak-base anion exchange resin DEAE cellulose, a successful quantitative batch-scale separation of Pt(IV) and Pd(II) from a large excess of various interfering cations and anions in chloride solutions is reported in this paper. DEAE adsorption decreased PGMs content to less than ICP-MS detection limit of 0.001 mg/L within 15 min with Pd(II) and Pt(IV) recoveries approximating 100% each. The results showed that the maximum loading capacity of the resin for Pt(IV) and Pd(II) can reach 32.57 and 36.86 mg/g, which represents 96 and 98% adsorption of Pt and Pd respectively, and 90.69% of the overall loading capacity.

The results also indicated that with only few bed volumes (2 to 4), using 0.05 M thiourea as eluant, > 99% of the adsorbed solutes could be successfully eluted; resulting in a small volume of highly concentrated PGMs eluate which is suitable for downstream processing. PGMs are then recovered from thiourea strip liquors by reduction-precipitation using alkali metal borohydride e.g. NaBH₄. In order to minimize resin handling and associated resin losses, adsorption and elution may be performed in a same column. With the development of the flowsheet herein by The Western Australian School of Mines, substantial PGM recoveries from oxide and mixed oxide/sulfide ores are now possible. The technique is meant to be a direct treatment route from flotation concentrate to PGM refinery feed.

Acknowledgments

The authors would like to thank Curtin International Postgraduate Research Scholarships (CIPRS) at Curtin University in Perth, Western Australia for funding this project and allowing the publication of its results and also thank Panoramic Resources Plc. for supplying ore samples. The financial support from the Mineral Research Institute of Western Australia (MRIWA Grant M458) is also much appreciated. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

Appendix A

Table A.1
Coefficients generated from the fitting of Langmuir and Freundlich isotherms.

Langmuir model			Freundlich model			
Element	r ²	r	z ^a	r ²	r	z ^a
Pt(IV)	0.894	0.946	1.788	0.990	0.995	2.993
Pd(II)	0.901	0.949	1.824	0.960	0.980	2.292

^a z-transform = 0.5 * [ln(1 + r) - ln(1 - r)].

Difference between z-transforms of the models for Pt = z_{Pt(L-F)} = 1.788–2.993 = –1.206.

Difference between z-transforms of the models for Pd = z_{Pd(L-F)} = 1.824–2.292 = –0.469.

With 10 samples per correlation coefficient, we can calculate the standard error of each difference:

$$\sigma_{Pt(L-F)} = \sqrt{\frac{1}{N_{Pt,L} - 3} + \frac{1}{N_{Pt,F} - 3}} = \sqrt{\frac{1}{10 - 3} + \frac{1}{10 - 3}} = 0.53$$

This means that the 95% confidence limit around the difference between the z-transforms of the metals would be:

Pt (IV) models

Lower limit Pt (95%): –1.206–1.96 * 0.53 = –2.25

Upper limit Pt (95%): –1.206 + 1.96 * 0.53 = –0.158

Since the sign of the upper and lower limits are the same, the difference between the two z-transforms is not zero and hence the difference between the corresponding correlation coefficients is also not zero, in other words one model is significantly better (95% confidence) than the other.

Pd (II) models

Lower limit Pd (95%): –1.206 – 1.96 * 0.82 = –1.52

Upper limit Pd (95%): –1.206 + 1.96 * 0.82 = 0.579

For Pd, the difference between the two models does not seem to be significant at a 95% confidence level and hence it is not possible to differentiate between the fits of the two models at a 95% confidence level.

References

- Adams, M.D., McDougall, G.J., Hancock, R.D., 1987. Models for the adsorption of auricyanide onto activated carbon. Part III: comparison between the extraction of auricyanide by activated carbon, polymeric adsorbents and 1-Pentanol. *Hydrometallurgy* 19, 95–115.
- Al-Bazi, S.J., Chow, A., 1984. Platinum metals-solution chemistry and separation methods (ion exchange and solvent extraction). *Talanta* 31 (10), 815–836.
- Awadalla, F.T., Molnar, R.E., Ritey, G.M., 1994. U.S. Patent No 5,304,233. Washington, DC: U.S. Patent and Trademark Office.
- Becker, M., Wiese, J., Ramonotsi, M., 2014. Investigation into the mineralogy and flotation performance of oxidised PGM ore. *Miner. Eng.* 65, 24–32.
- Bernardis, F.L., Grant, R.A., Sherrington, D.C., 2005. A review of methods of separation of the platinum-group metals through their chloro-complexes. *React. Funct. Polym.* 65 (3), 205–217.
- Bulatovic, S., 2003. Evaluation of alternative reagent schemes for the flotation of platinum group minerals from various ores. *Miner. Eng.* 16 (10), 931–939.
- Cabri, L.J., Wilhelmij, H.R., Eksteen, J.J., 2017. Contrasting mineralogical and processing potential of two mineralization types in the platinum group element and Ni-bearing Kapalagulu Intrusion, western Tanzania. *Ore Geol. Rev.* 90 (11), 772–789.
- Crundwell, F.K., 2013. The dissolution and leaching of minerals: mechanisms, myths and misunderstandings. *Hydrometallurgy* 139, 132–148.
- Crundwell, F.K., Moats, M., Ramachandran, V., 2011. *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals*. Elsevier.
- Dabrowski, A., 2001. Adsorption-from theory to practice. *Adv. Colloid Interf. Sci.* 93, 135–224.
- Davidson, R.J., Schmidt, C.G., 1986. A Review of the AARL process for the elution of gold from activated carbon. In: 13th CMMI Congress 4, pp. 215–225.
- Demopoulos, G.P., 1989. Refining of platinum-group metals. *Can. Min. Metall. Bull.* 82 (923), 165–171.
- Dyosi, Z., McCrindle, R.L., Wondimu, T., Botha, B.M., Ndirbewu, P.P., 2009. The use of Dowex-M43 ion exchange resin in the determination of Pt and Pd in converter matte by ICP-OES. *S. Afr. J. Chem.* 62, 5.
- Evans, D.M., 2002. Potential for bulk mining of oxidized platinum-group element deposits. *Appl. Earth Sci.* 111 (1), 81–86.
- Fleming, C.A., Cromberge, G., 1984. The extraction of gold from cyanide solutions by strong-and weak-base anion exchange resins. *J. South. Afr. Inst. Min. Metall.* 84 (5), 125–137.
- Fleming, C.A., Nicol, M.J., 1984. The absorption of gold cyanide onto activated carbon. III. Factors Influencing the Rate of Loading and the Equilibrium Capacity. *J. South. Afr. Inst. Min. Metall.* 84 (4), 85–93.
- Fontàs, C., Hidalgo, M., Salvadó, V., 2009. Adsorption and Preconcentration of Pd(II), Pt(IV), and Rh(III) using anion-exchange solid-phase extraction cartridges (SPE). *Solvent Extr. Ion Exc.* 27 (1), 83–96.
- Gaita, R., Al-Bazi, S.J., 1995. An ion exchange method for selective separation of palladium, platinum and rhodium from solutions obtained by leaching automotive catalytic converters. *Talanta* 42 (2), 249–255.
- Godlewska-żytkiewicz, B., 2004. Preconcentration and Separation Procedures for the Spectrochemical Determination of Platinum and Palladium. *Microchim. Acta* 147 (4), 189–210.
- Gorsuch, R.L., Lehmann, C.S., 2010. Correlation coefficients: mean bias and confidence interval distortions. *J. Meth. Meas. Soc. Sci.* 1 (2), 52–65.
- Ishida, K., Kiriya, T., Kuroda, R., 1968. Separation of platinum and palladium from base metals with a weakly basic cellulose ion exchanger. *Anal. Chim. Acta* 41, 537–545.
- Kaminski Jr., E.E., 1970. Anion Exchange Separations of Metal Ions in Thiocyanate Media. Iowa State University of Science and Technology, United State of America (PhD Thesis).
- Koch, K.R., Burger, M.R., Kramer, J., Westra, A.N., 2006. ¹⁹⁵Pt NMR and DFT computational methods as tools towards the understanding of speciation and hydration/solvation of [PtX₆]²⁻ (X = Cl⁻, Br⁻) anions in solution. *Dalton Trans.* (27), 3277–3284.
- Kononova, O.N., Melnikov, A.M., Duba, E.V., 2014. Sorption and separation of platinum and rhodium in presence of transition metals. *J. Siberian Federal Univ. Chem.* 2 (7), 170–184.
- Kraemer, D., Junge, M., Oberthür, T., Bau, M., 2015. Improving recoveries of platinum and palladium from oxidized Platinum-Group Element ores of the Great Dyke, Zimbabwe, using the biogenic siderophore Desferrioxamine B. *Hydrometallurgy* 152, 169–177.
- Kraemer, D., Junge, M., Bau, M., 2017. Oxidized ores as future resource for platinum group metals: current state of research. *Chem. Ing. Tech.* 89 (1–2), 53–63.
- Kumar, S., Jain, S., 2013. History, introduction, and kinetics of ion exchange materials. *J. Chem.* 2013.
- Kuroda, R., Kiriya, T., Ishida, K., 1968. A specific method for the separation of mercury (II) using a weakly basic cellulose ion exchanger. *Anal. Chim. Acta* 40, 305–310.
- Kyriakakis, G., 2005. Extraction of gold from platinum group metal (PGM) ores. *Dev. Miner. Process.* 15, 897–917.
- Lewins, J., Greenaway, T., 2004. The Pantan Platinum-Palladium Project. The Australian Institute of Mining and Metallurgy Bulletin (July–August 04).
- McKevitt, B.R., 2007. Removal of Iron by Ion Exchange from Copper Electrowinning Electrolyte Solutions Containing Antimony and Bismuth. University of British Columbia, Canada (Doctoral dissertation).
- Mpinga, C.N., Eksteen, J.J., Aldrich, C., Dyer, L., 2017a. Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore. *Miner. Eng.* 110, 153–165.
- Mpinga, C.N., Eksteen, J.J., Aldrich, C., Dyer, L., 2017b. Atmospheric Leach Process of High-Chromitite PGM-Bearing Ores in Oxidised Mineralisation through a Single-Stage and two-Stage Techniques. (Revised paper under review).
- Nikoloski, A.N., Ang, K.L., 2014. Review of the application of ion exchange resins for the

- recovery of platinum-group metals from hydrochloric acid solutions. *Miner. Process. Extr. Metall. Rev.* 35 (6), 369–389.
- Nikoloski, A.N., Ang, K.L., Li, D., 2015. Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins. *Hydrometallurgy* 152, 20–32.
- Oberthür, T., Melcher, F., Buchholz, P., Locmelis, M., 2013. The oxidized ores of the main sulphide zone, Great Dyke, Zimbabwe: turning resources into minable reserves-mineralogy is the key. *J. South. Afr. Inst. Min. Metall.* 113 (3), 191–201.
- Paunovic, M., Schlesinger, M., 2006. *Fundamentals of Electrochemical Deposition*. Vol. 45 John Wiley & sons.
- Pesavento, M., Sturini, M., D'Agostino, G., Biesuz, R., 2010. Solid phase extraction of copper (II) by fixed bed procedure on cation exchange complexing resins. *J. Chromatogr. A* 1217 (8), 1208–1218.
- SenthilKumar, P., Ramalingam, S., Abhinaya, R.V., Kirupha, S.D., Vidhyadevi, T., Sivanesan, S., 2012. Adsorption equilibrium, thermodynamics, kinetics, mechanism and process design of zinc (II) ions onto cashew nut shell. *Can. J. Chem. Eng.* 90 (4), 973–982.
- Shams, K., Goodarzi, F., 2006. Improved and selective platinum recovery from spent α -alumina supported catalysts using pretreated anionic ion exchange resin. *J. Hazard. Mater.* 131 (1), 229–237.
- Smith, B., Moody, P., 1991. The Use of DEAE-Cellulose to Extract Anionic Organic Material from Groundwaters. EUR, Luxembourg.
- Waitz Jr., H.W., 1982. Ion exchange for recovery of precious metals. *Plat. Surf. Finish.* 69 (4), 56–59.
- Warszawsky, A., 1983. Ion exchange separation of platinum and palladium by nucleophilic displacement with thiocyanate or thiourea^{1,2}. *Sep. Purif. Methods* 12 (1), 37–48.
- Weber, D., 1997. Method Development in Solid Phase Extraction using ISOLUTE® SAX and ISOLUTE PE-AX SPE Columns for the Extraction of Aqueous Samples. (Technical note 103).
- Zhou, L., Liu, J., Liu, Z., 2009. Adsorption of platinum(IV) and palladium(II) from aqueous solution by thiourea-modified chitosan microspheres. *J. Hazard. Mater.* 172, 439–446.
- Zipperian, D.C., Raghavan, S., 1985. The recovery of vanadium from dilute acid sulfate solutions by resin ion exchange. *Hydrometallurgy* 13 (3), 265–281.
- Zolgharnein, J., Shahmoradi, A., 2010. Adsorption of Cr(VI) onto *Elaeagnus* tree leaves: statistical optimization, equilibrium modeling, and kinetic studies. *J. Chem. Eng. Data* 55 (9), 3428–3437.

APPENDICES

The section includes:

- **Appendix A** providing the signed statement of contribution of co-authors.
- **Appendix B** providing at first hand equipment used in this thesis.
- **Appendix C** providing the certificate of origin and analysis — The safety data sheet of weak-base anion exchange resin DEAE cellulose used for adsorption tests.
- **Appendix D** providing supporting calculations derived from synthetic stock solutions preparation. These solutions were used for adsorption tests.
- **Appendix E** giving the tabulation of experimental data.

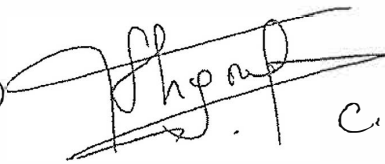
APPENDIX A: SIGNED STATEMENT OF CONTRIBUTION OF CO-AUTHORS.

To Whom It May Concern

I, **Cleophace Ngoie Mpinga**, contributed with the conception, design, analysis and interpretation of experimental data and wrote all four papers reported in the thesis. These are:

- **C.N. Mpinga**, J.J. Eksteen, C. Aldrich, L. Dyer. 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review. *Minerals Engineering* 78, 93-113.
- **Cleophace Ngoie Mpinga**, Jacques Eksteen, Chris Aldrich, Laurence Dyer. 2017. Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore. *Minerals Engineering* 110, 153-165.
- **Cleophace Ngoie Mpinga**, Jacques Eksteen, Chris Aldrich, Laurence Dyer. 2018. Atmospheric leach process of high-chromitite PGM-bearing oxidized mineralized ore through a single-stage and two-stage techniques. *Minerals Engineering* 125, 165-175.
- **Cleophace Ngoie Mpinga**, Jacques Eksteen, Chris Aldrich, Laurence Dyer. 2018. A conceptual hybrid process flowsheet for platinum group metals (PGMs) recovery from a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization through a single-stage leach and adsorption onto ion exchange resin. *Hydrometallurgy* 178, 88-96.

(Signature of Candidate)

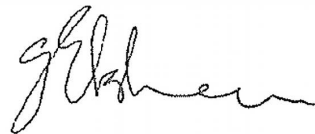


C.N. Mpinga

Friday 15th June 2018

I, as a co-author, endorse that this level of contribution by the candidate indicated above is appropriate.

Prof. Jacques Eksteen (Signature of co-author 1)



15/6/2018.

Prof. Chris Aldrich (Signature of co-author 2)



15/6/2018

Dr. Laurence Dyer (Signature of co-author 3)

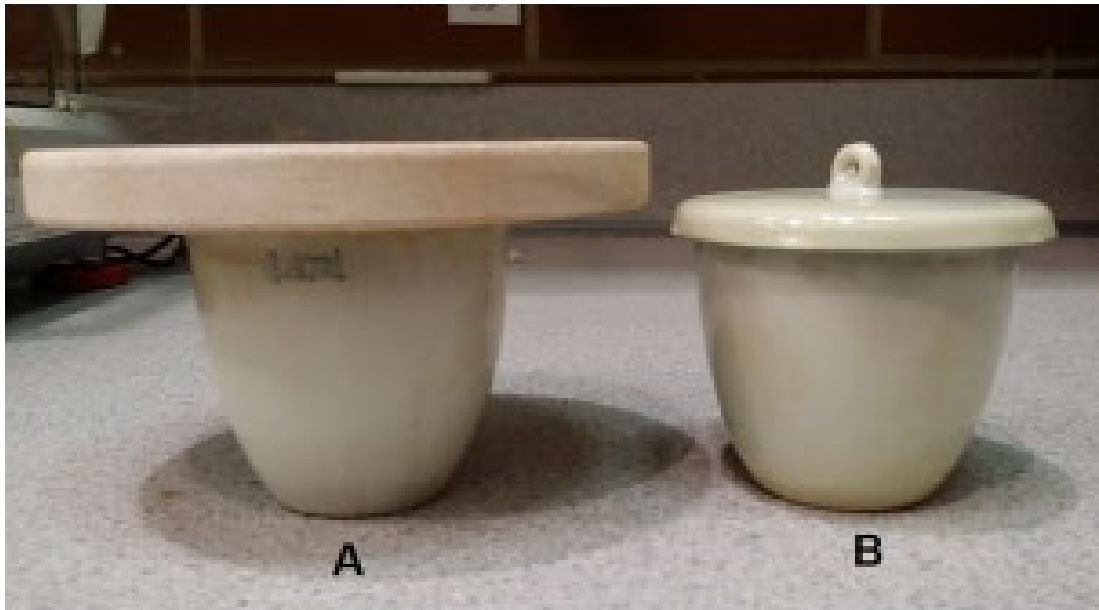


16/6/2018

APPENDIX B: AT FIRST HAND EQUIPMENT USED IN THIS THESIS.

B1. EQUIPMENT USED AT ROASTING STAGE

Appendix B1.1.



Porcelain crucibles and lids used in this study: (A) alumina lid weighs 405 g and (B) porcelain lid weighs 24 g

Appendix B1.2.



Unroasted sticky paste-like material derived from ground run-of-mine ore mixed with H_2SO_4 , CaCl_2 or MgCl_2

Appendix B1.3.



Static-air muffle furnace equipped with a programmable temperature controller

B2. EQUIPMENT USED AT LEACHING STAGE



Experimental setup at leaching stage: (1) Thermostated water-bath, (2) IKA Eurostar variable speed overhead mechanical stirrer (3) Batch reactor with conical bottom (4) Transfer tube for adding oxygen, (5) Cooling reflux condenser connected to a chilled water line

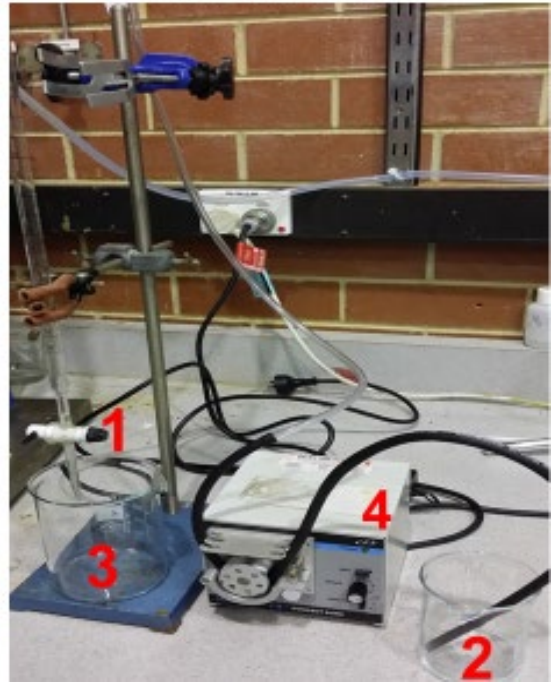
B3. EQUIPMENT USED AT ADSORPTION AND ELUTION STAGES

Appendix B3.1.



Experimental setup at adsorption stage: Open-ended rolling bottles rotated at 105 rpm

Appendix B3.2.



Experimental setup at elution stage: (1) Glass column packed with loaded resin, (2) Eluant reservoir, (3) Eluate collection tank, (4) Peristaltic pump

Appendix B3.3.



pH meter WP-80 with probes (1), (2) and (3) for measuring solution pH, Eh and temperature

APPENDIX C: CERTIFICATE OF ORIGIN AND ANALYSIS — SAFETY DATA SHEET OF WEAK-BASE ANION EXCHANGE RESIN DEAE CELLULOSE.



Certificate Of Origin

Catalogue Number: D199050

Chemical Name: DEAE-Cellulose, (approx. 70% moisture content)

Synonym: Cellulose-DEAE, Diethylaminoethyl-cellulose

CAS Number: 9013-34-7

Molecular Formula: C₂₀H₂₃NO₅



This hereby is to certify the above-mentioned product is Chemical, organic synthesized only and no material of animal or biological origin was used in the synthesizing processes or came in contact with all equipment and reagent media used during processing, purification and storage.

The chemical above was manufactured by Toronto Research Chemicals Inc, Toronto, ON, Canada, M3J2J8.

Andrew Wang

Shipping Manager
Toronto Research Chemicals Inc.
2 Brisbane Rd
Toronto, ON
Canada, M3J2J8

CERTIFICATE OF ANALYSIS

2 Brisbane Road, Toronto, ON. M3J 2J8 Canada Tel: (416) 665-9696 Fax: (416) 665-4439 E-mail: orders@trc-canada.com Website: www.trc-canada.com

1. Identification

CAS Number:

9013-34-7

Catalogue Number:

D199050

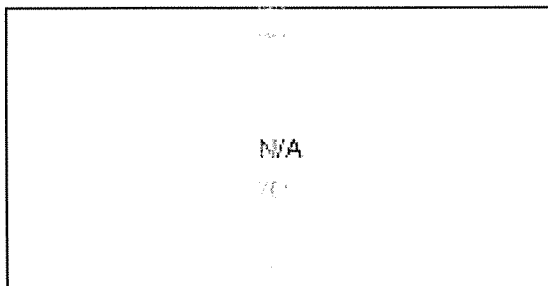
Product:

DEAE-Cellulose, (approx. 70% moisture content)

Synonyms:

Cellulose-DEAE, Diethylaminoethyl-cellulose

Structure:



Molecular Formula:

$C_{20}H_{23}NO_5$

Molecular Weight:

N/A

Source of Product:

N/A

2. Analytical Information

Lot Number:

8-JTN-131-1

Melting Point:

N/A

Boiling Point:

N/A

Atmosphere:

Air

Appearance of Product:

Off-White Solid

Solubility

N/A

Method for Determining Identity:

N/A

Stability

Not Determined

Purity:

~1-1.5 meq/g

Long Term Storage Condition:

Refrigerator

Additional Information:

Elemental Analysis: (Found) %C: 17.06, %H: 8.51, %N: 0.56
Water Content: 62.6% by Karl Fischer



Philip Chan, Head of Quality Assurance

QC Test Date

October 1, 2015

Retest Date

September 29, 2018



Safety Data Sheet - Version 5.0

Preparation Date 6/13/2014

Latest Revision Date (If Revised)

SDS Expiry Date 6/11/2017

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product Identifier

Chemical Name **DEAE-Cellulose** (approx. 70% moisture content)

Catalogue # D199050

1.2 Relevant Identified Uses of the Substance or Mixture and Uses Advised Against

Product Uses To be used only for scientific research and development. Not for use in humans or animals.

1.3 Details of the Supplier of the Safety Data Sheet

Company Toronto Research Chemicals
2 Brisbane Road
Toronto, ON M3J 2J8
CANADA

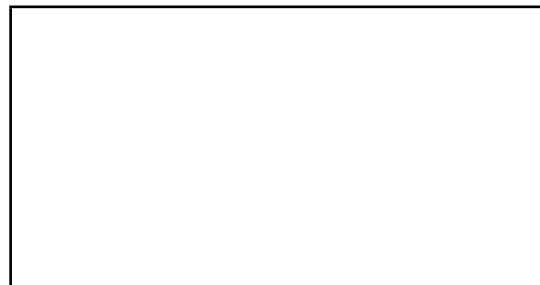
Telephone +14166659696

FAX +14166654439

Email **orders@trc-canada.com**

1.4 Emergency Telephone Number

Emergency# +14166659696 between 0800-1700 (GMT-5)



2. HAZARDS IDENTIFICATION

WHMIS Symbols (Canada)

WHMIS Classification (Canada)

None Not WHMIS controlled.

2.1/2.2 Classification of the Substance or Mixture and Label Elements

GHS Hazards Classification (According to EU Regulation 1272/2008 and US OSHA 1910.1200)

Not a hazardous substance by GHS.

EU Classification (According to EU Regulation 67/548/EEC)

Not a hazardous substance by this Classification.

EU Risk and Safety Statements (According to EU Regulation 67/548/EEC)

Hazard Statements Hazard Codes

None

Risk Codes and Phrases

None Not a hazardous substance by this Classification.

Safety Precaution Codes and Phrases

GHS Hazards Identification (According to EU Regulation 1272/2008 and US OSHA 1910.1200)

Signal Word None

GHS Hazard Statements

None Not a hazardous substance according to GHS.

GHS Precautionary Statements

2.3 Unclassified Hazards/Hazards Not Otherwise Classified

No data available

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Molecular Formula: C₂₀H₂₃NO₅

Molecular Weight:

CAS Registry #: 9013-34-7

EC#:

Synonyms

Cellulose-DEAE, Diethylaminoethyl-cellulose

3.2 Mixtures

Not a mixture.

4. FIRST AID MEASURES

4.1 Description of First Aid Measures

General Advice

If medical attention is required, show this safety data sheet to the doctor.

If Inhaled

If inhaled, move casualty to fresh air. If not breathing, give artificial respiration and consult a physician.

In Case of Skin Contact

Wash affected area with soap and water. Consult a physician if any exposure symptoms are observed.

In Case of Eye Contact

Immediately rinse eyes with plenty of water for at least 15 minutes. Consult a physician.

If Swallowed

Never give anything by mouth to an unconscious person. Rinse mouth with water. Do NOT induce vomiting unless advised to do so by a physician or Poison Control Center. Seek medical attention.

4.2 Most Important Symptoms and Effects, Both Acute and Delayed

No data available

4.3 Indication of any Immediate Medical Attention and Special Treatment Needed

No data available

5. FIREFIGHTING MEASURES

5.1 Extinguishing Media

Suitable Extinguishing Media

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special Hazards Arising from the Substance or Mixture

Carbon oxides, Nitrogen oxides

5.3 Advice for Firefighters

Wear self contained breathing apparatus for fire fighting if necessary.

5.4 Further Information

No data available

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal Precautions, Protective Equipment and Emergency Procedures

Use recommended personal protective equipment (see Section 8). Prevent the formation of dusts and mists. Adequate ventilation must be provided to ensure dusts or mists are not inhaled.

6.2 Environmental Precautions

Material should not be allowed to enter the environment. Prevent further spillage or discharge into drains, if safe to do so.

6.3 Methods and Materials for Containment and Cleaning Up

Contain the spill and then collect using non-combustible absorbent material (such as clay, diatomaceous earth, vermiculite or other appropriate material). Place material in a suitable, sealable container and then dispose according to local/national regulations and guidance (see Section 13).

For protective equipment, refer to Section 8. For disposal, see Section 13.

7. HANDLING AND STORAGE

7.1 Precautions for Safe Handling

Avoid contact with skin and eyes. Ventilation and proper handling are to be used to prevent the formation of dusts and mists. Normal measures for preventative fire protection. No smoking, eating or drinking around this material. Wash hands after use.

7.2 Conditions for Safe Storage, Including any Incompatibilities

Ensure container is kept securely closed before and after use. Keep in a well ventilated area and do not store with strong oxidizers or other incompatible materials (see Section 10).

Storage conditions: Refrigerator

7.3 Specific End Uses

For scientific research and development only. Not for use in humans or animals.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control Parameters

Contains no components with established occupational exposure limits.

8.2 Exposure Controls

Appropriate Engineering Controls

A laboratory fumehood or other appropriate form of local exhaust ventilation should be used to avoid exposure.

Personal Protective Equipment

All recommendations below are advisory in nature and a risk assessment should be performed by the employer/end user prior to use of this product. The type of protective equipment must be selected based on the amount and concentration of the dangerous material being used in the workplace.

Eye/Face Protection

Safety glasses or safety goggles. All equipment should have been tested and approved under appropriate standards, such as NIOSH (US), CSA (Canada), or EN 166 (EU).

Skin Protection

Gloves should be used when handling this material. Gloves are to be inspected prior to use. Contaminated gloves are to be removed using proper glove removal technique so that the outer surface of the glove does not contact bare skin. Dispose of contaminated gloves after use in compliance with good laboratory practices and local requirements.

Gloves used for incidental exposures (splash protection) should be designated as "low chemical resistant" or "waterproof" by EU standard EN 374. Unrated gloves are not recommended.

Suggested gloves: AnsellPro nitrile gloves style 92-500 or 92-600, 5 mil thickness.

Penetration time has not been determined.

Gloves used for prolonged direct exposure (immersion) should be designated "chemical resistant" as per EN 734 with the resistance codes corresponding to the anticipated use of the material.

Suggested gloves: AnsellPro Viton/Butyl gloves style 38-612, 4/8 mil thickness.

Penetration time has not been determined.

These recommendations may not apply if the material is mixed with any other chemical, or dissolved into a solution. A risk assessment must be performed to ensure the gloves will still offer acceptable protection.

Body Protection

Fire resistant (Nomex) lab coat or coveralls.

Respiratory Protection

Recommended respirators are NIOSH-approved N95 or CEN-approved FFP2 particulate respirators. These are to be only used as a backup to local exhaust ventilation or other engineering controls. If the respirator is the only means of protection, a full-face supplied air respirator must be used.

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on Basic Physical and Chemical Properties

A) Appearance

Light Grey Solid

B) Odour

No data available

C) Odour Threshold

D) pH

No data available

E) Melting Point/Freezing Point

No data available

G) Flash point

No data available

I) Flammability (Solid/Gas)

No data available

K) Vapour Pressure

No data available

M) Relative Density

No data available

O) Partition Coefficient: n-octanol/water

No data available

Q) Decomposition Temperature

No data available

S) Explosive Properties

No data available

No data available

F) Initial Boiling Point/Boiling Range

No data available

H) Evaporation Rate

No data available

J) Upper/Lower Flammability/Explosive Limits

No data available

L) Vapour Density

No data available

N) Solubility

N/A

P) Auto-Ignition Temperature

No data available

R) Viscosity

No data available

T) Oxidizing Properties

No data available

9.2 Other Information

no data available

10. STABILITY AND REACTIVITY

10.1 Reactivity

No data available

10.2 Chemical Stability

Stable under recommended storage conditions.

10.3 Possibility of Hazardous Reactions

No data available

10.4 Conditions to Avoid

No data available

10.5 Incompatible Materials

Strong oxidizing agents.

10.6 Hazardous Decomposition Products

No data available

11. TOXICOLOGICAL INFORMATION

11.1 Information on Toxicological Effects

A) Acute Toxicity

No data available

B) Skin Corrosion/Irritation

No data available

C) Serious Eye Damage/Irritation

No data available

D) Respiratory or Skin Sensitization

No data available

E) Germ Cell Mutagenicity

No data available

F) Carcinogenicity

No data available

G) Reproductive Toxicity/Teratogenicity

No data available

H) Single Target Organ Toxicity - Single Exposure

No data available

I) Single Target Organ Toxicity - Repeated Exposure

No data available

J) Aspiration Hazard

No data available

K) Potential Health Effects and Routes of Exposure

Inhalation

May be harmful if inhaled. May cause respiratory tract irritation.

Ingestion

May be harmful if swallowed.

Skin

May be harmful if absorbed through skin. May cause skin irritation.

Eyes

May cause eye irritation.

L) Signs and Symptoms of Exposure

No data available

To the best of our knowledge, the chemical, physical, and toxicological properties of this material have not been thoroughly investigated.

M) Additional Information

RTECS: Not listed

12. ECOLOGICAL INFORMATION

12.1 Toxicity

No data available

12.2 Persistence and Degradability

No data available

12.3 Bioaccumulative Potential

No data available

12.4 Mobility in Soil

No data available

12.5 Results of PBT and vPvB Assessment

No data available

12.6 Other Adverse Effects

No data available

13. DISPOSAL CONSIDERATIONS

13.1 Waste Treatment Methods

A) Product

Product may be burned in an incinerator equipped with afterburner and scrubber. Excess and expired materials are to be offered to a licensed hazardous material disposal company. Ensure that all Federal and Local regulations regarding the disposal and destruction of this material are followed.

B) Contaminated Packaging

Dispose of as above.

C) Other Considerations

Product is not to be disposed of in sanitary sewers, storm sewers, or landfills.

14. TRANSPORT INFORMATION

14.1 UN Number

DOT (US): N/A

IATA: N/A

IMDG: N/A

ADR/RID: N/A

14.2 UN Proper Shipping Name

DOT (US)/IATA:

Not dangerous goods

IMDG/ARD/RID:

Not dangerous goods

14.3 Transport Hazard Class(es)

DOT (US): N/A

IATA: N/A

IMDG: N/A

ADR/RID: N/A

14.4 Packing Group

DOT (US): N/A

IATA: N/A

IMDG: N/A

ADR/RID: N/A

14.5 Environmental Hazards

DOT (US): None

IATA: None

IMDG: None

ADR/RID: None

14.6 Special Precautions for User

None

15. REGULATORY INFORMATION

This safety data sheet complies with the requirements of WHMIS (Canada), OSHA 1910.1200 (US), and EU Regulation EC No. 1907/2006 (European Union).

15.1 Safety, Health and Environmental Regulations/Legislation Specific for the Substance or Mixture

A) Canada

DSL/NDSL Status: This product is not listed on the Canadian DSL/NDSL.

B) United States

TSCA Status: This product is not listed on the US EPA TSCA.

C) European Union

ECHA Status: This product is not registered with the EU ECHA.

15.2 Chemical Safety Assessment

No data available

16. OTHER INFORMATION

16.1 Revision History

Original Publication Date: 6/13/2014

16.2 List of Abbreviations

LD50	Median lethal dose of a substance required to kill 50% of a test population.
LC50	Medial lethal concentration of a substance required to kill 50% of a test population.
LDLo	Lowest known lethal dose
TDLo	Lowest known toxic dose
IARC	International Agency for Research on Cancer
NTP	National Toxicology Program
RTECS	Registry of Toxic Effects of Chemical Substances

16.3 Further Information

Copyright 2013. Toronto Research Chemicals Inc. Copies may be made for internal use only. The above information is believed to be correct to the best of our knowledge, but is to be only used as a guide. To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated. Please take all due care when handling this product.

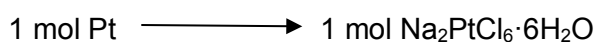
APPENDIX D: SUPPORTING CALCULATIONS DERIVED FROM SYNTHETIC STOCK SOLUTIONS PREPARATION. THESE SOLUTIONS WERE USED FOR ADSORPTION TESTS.

PREPARATION OF SYNTHETIC STOCK SOLUTIONS

1. Platinum concentration in stock solutions

$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ purity = 98%, $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ molar mass = 561.87 g/mol, Solution

$$\text{volume} = 1 \text{ L}, \text{ Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100$$



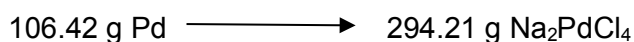
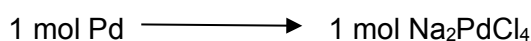
$$1 \text{ g of pure Pt} \longrightarrow \frac{561.87 \times 100}{195.08 \times 98} = 2.939 \text{ g Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$$

$$5 \text{ mg Pt} \longrightarrow \frac{2939 \times 5}{1000} = 14.695 \text{ mg Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} \text{ to be dissolved in 1 L.}$$

2. Palladium concentration in stock solutions

Na_2PdCl_4 purity = 98%, Na_2PdCl_4 molar mass = 294.21 g/mol, Solution

$$\text{volume} = 1 \text{ L}, \text{ Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100$$



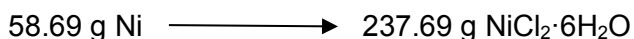
$$1 \text{ g of pure Pd} \longrightarrow \frac{294.21 \times 100}{106.42 \times 98} = 2.821 \text{ g Na}_2\text{PdCl}_4$$

$$5 \text{ mg Pd} \longrightarrow \frac{2821 \times 5}{1000} = 14.105 \text{ mg Na}_2\text{PdCl}_4 \text{ to be dissolved in 1 L.}$$

3. Nickel concentration in stock solutions

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ purity = 98%, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ molar mass = 237.69 g/mol, Solution

$$\text{volume} = 1 \text{ L}, \text{ Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100$$

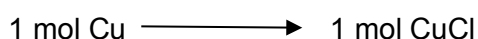


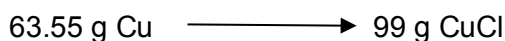
$$1 \text{ g of pure Ni} \longrightarrow \frac{237.69 \times 100}{58.69 \times 98} = 4.133 \text{ g NiCl}_2 \cdot 6\text{H}_2\text{O} \text{ to be dissolved in 1 L.}$$

4. Copper concentration in stock solutions

CuCl purity = 98%, CuCl molar mass = 99 g/mol, Solution volume = 1 L,

$$\text{Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100$$



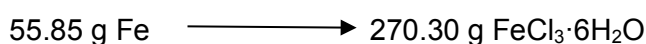
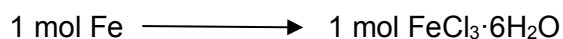


1 g of pure Cu \longrightarrow $\frac{99 \times 100}{63.55 \times 98} = 1.590 \text{ g}$ CuCl to be dissolved in 1 L.

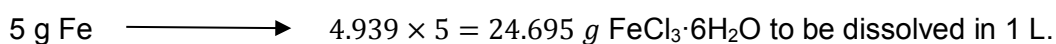
5. Iron concentration in stock solutions

FeCl₃·6H₂O purity = 98%, FeCl₃·6H₂O molar mass = 270.30 g/mol, Solution

volume = 1 L, $Purity (\%) = \frac{Pure\ mass}{Sample\ mass} \times 100$



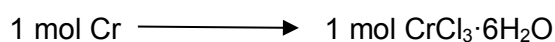
1 g of pure Fe \longrightarrow $\frac{270.30 \times 100}{55.85 \times 98} = 4.939 \text{ g}$ FeCl₃·6H₂O



6. Chromium concentration in stock solutions

CrCl₃·6H₂O purity = 96%, CrCl₃·6H₂O molar mass = 266.45 g/mol, Solution

volume = 1 L, $Purity (\%) = \frac{Pure\ mass}{Sample\ mass} \times 100$



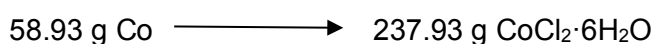
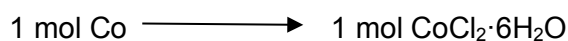
1 g of pure Cr \longrightarrow $\frac{266.45 \times 100}{52 \times 96} = 5.338 \text{ g}$ CrCl₃·6H₂O

100 mg Cr \longrightarrow $\frac{5338 \times 100}{1000} = 533.8 \text{ mg}$ CrCl₃·6H₂O to be dissolved in 1 L.

7. Cobalt concentration in stock solutions

CoCl₂·6H₂O purity = 98%, CoCl₂·6H₂O molar mass = 237.93 g/mol, Solution

volume = 1 L, $Purity (\%) = \frac{Pure\ mass}{Sample\ mass} \times 100$



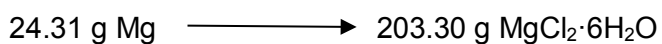
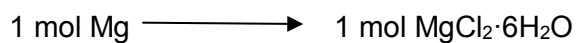
1 g of pure Co \longrightarrow $\frac{237.93 \times 100}{58.93 \times 98} = 4.12 \text{ g}$ CoCl₂·6H₂O

50 mg Co \longrightarrow $\frac{4120 \times 50}{1000} = 206 \text{ mg}$ CoCl₂·6H₂O to be dissolved in 1 L.

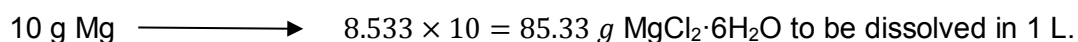
8. Magnesium concentration in stock solutions

MgCl₂·6H₂O purity = 98%, MgCl₂·6H₂O molar mass = 203.30 g/mol, Solution

$$\text{volume} = 1 \text{ L, } \text{Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100$$



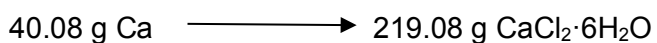
$$1 \text{ g of pure Mg} \longrightarrow \frac{203.30 \times 100}{24.31 \times 98} = 8.533 \text{ g MgCl}_2 \cdot 6\text{H}_2\text{O}$$



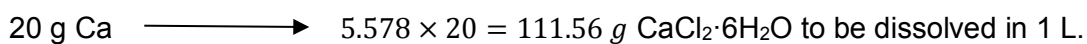
9. Calcium concentration in stock solutions

CaCl₂·6H₂O purity = 98%, CaCl₂·6H₂O molar mass = 219.08 g/mol, Solution

$$\text{volume} = 1 \text{ L, } \text{Purity (\%)} = \frac{\text{Pure mass}}{\text{Sample mass}} \times 100$$



$$1 \text{ g of pure Ca} \longrightarrow \frac{219.08 \times 100}{40.08 \times 98} = 5.578 \text{ g CaCl}_2 \cdot 6\text{H}_2\text{O}$$



APPENDIX E: TABULATION OF EXPERIMENTAL DATA.

TEST 1							
Mass solid: 200 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[H ₂ SO ₄]: 1 M Roasting time: 15 minutes Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	98.85	99.90	105.50	108.31	113.57
	Ni	0	428.05	429.97	447.39	453.22	491.97
	Cr	0	663.52	673.92	707.20	715.52	757.12
	Fe	0	2956.64	2994.72	3133.44	3157.92	3386.40
	Pt	0	0.00	0.00	0.00	0.00	0.00
	Pd	0	0.00	0.00	0.00	0.00	0.00
PERCENTAGE LEACHED	Cu	0	76.51	77.32	81.66	83.83	87.90
	Ni	0	69.04	69.35	72.16	73.10	79.35
	Cr	0	3.19	3.24	3.40	3.44	3.64
	Fe	0	10.87	11.01	11.52	11.61	12.45
	Pt	0	0.06	0.06	0.00	0.00	0.11
	Pd	0	0.10	0.08	0.03	0.03	0.08

TEST 2							
Mass solid: 200 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[H ₂ SO ₄]: 1 M Roasting time: 15 minutes Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	111.20	117.22	123.24	125.38	128.21
	Ni	0	443.05	541.45	551.30	561.16	571.02
	Cr	0	636.48	655.20	678.08	696.80	746.72
	Fe	0	2975.68	3065.44	3182.40	3244.96	3541.44
	Pt	0	0.00	0.00	0.00	0.00	0.00
	Pd	0	0.00	0.00	0.00	0.00	0.00
PERCENTAGE LEACHED	Cu	0	86.07	90.73	95.39	97.04	99.23
	Ni	0	71.46	87.33	88.92	90.51	92.10
	Cr	0	3.06	3.15	3.26	3.35	3.59
	Fe	0	10.94	11.27	11.70	11.93	13.02
	Pt	0	0.08	0.00	0.04	0.03	0.03
	Pd	0	0.05	0.05	0.07	0.02	0.05

TEST 3							
Mass solid: 200 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[H ₂ SO ₄]: 1 M Roasting time: 15 minutes Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	107.61	109.01	112.87	116.02	123.73
	Ni	0	443.55	455.14	468.72	488.13	534.56
	Cr	0	657.28	661.44	705.12	721.76	765.44
	Fe	0	3182.40	3209.60	3372.80	3448.96	3674.72
	Pt	0	0.00	0.00	0.00	0.00	0.00
	Pd	0	0.00	0.00	0.00	0.00	0.00
PERCENTAGE LEACHED	Cu	0	83.29	84.37	87.36	89.80	95.77
	Ni	0	71.54	73.41	75.60	78.73	86.22
	Cr	0	3.16	3.18	3.39	3.47	3.68
	Fe	0	11.70	11.80	12.40	12.68	13.51
	Pt	0	0.05	0.00	0.03	0.03	0.00
	Pd	0	0.03	0.03	0.05	0.03	0.03

TEST 4							
Mass solid: 50 g Solution volume: 1000 mL Solution pH: 2 Rotational rate: 600 rpm				[SCN]: 40 g/L Leaching temperature: 50°C Oxygen addition: 0.1 mL/min.			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	1	0,9	1	1	1
	Ni	0	4,2	4,2	4,7	5,2	7,7
	Cr	0	12	10,8	10,9	10,6	10,8
	Fe	0	31,6	26,4	28,4	28	29,4
	Pt	0	0,00045	0,00025	0,0002	0,0006	0,00055
	Pd	0	0,0528	0,072	0,0877	0,0909	0,0965
PERCENTAGE LEACHED	Cu	0	10,00	9,00	10,00	10,00	10,00
	Ni	0	7,00	7,00	7,83	8,67	12,83
	Cr	0	0,06	0,06	0,06	0,06	0,06
	Fe	0	0,23	0,19	0,20	0,20	0,21
	Pt	0	0,22	0,12	0,10	0,29	0,27
	Pd	0	18,27	24,91	30,35	31,45	33,39

TEST 5							
Mass solid: 50 g Solution volume: 1000 mL Solution pH: 2 Rotational rate: 600 rpm				[SCN]: 40 g/L Leaching temperature: 85°C Oxygen addition: 0.1 mL/min.			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	0,2	0,1	0,3	0,2	0,2
	Ni	0	1,3	1,5	2,3	2,4	5,3
	Cr	0	2,5	0,9	1,8	1,9	3,3
	Fe	0	8,6	2,6	5,8	6,2	7
	Pt	0	0,00085	0,0009	0,001	0,00145	0,00155
	Pd	0	0,0329	0,0378	0,0408	0,042	0,0507
PERCENTAGE LEACHED	Cu	0	2,00	1,00	3,00	2,00	2,00
	Ni	0	2,17	2,50	3,83	4,00	8,83
	Cr	0	0,01	0,00	0,01	0,01	0,02
	Fe	0	0,06	0,02	0,04	0,04	0,05
	Pt	0	0,42	0,44	0,49	0,71	0,76
	Pd	0	11,38	13,08	14,12	14,53	17,54

TEST 6							
Mass solid: 50 g Solution volume: 1000 mL Solution pH: 2 Rotational rate: 600 rpm				[SCN]: 40 g/L + 1 g/L I(I) Leaching temperature: 50°C Oxygen addition: 0.1 mL/min.			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	0,1	0,1	0,1	0	0,1
	Ni	0	0,8	0,7	1,4	2,2	5,2
	Cr	0	0,2	0,3	0,3	0,4	0,5
	Fe	0	1,4	1,6	1,8	2	3,4
	Pt	0	0,00025	0,00005	0,0001	0,00015	0,00025
	Pd	0	0,0058	0,0029	0,0031	0,0062	0,0273
PERCENTAGE LEACHED	Cu	0	1,00	1,00	1,00	0,00	1,00
	Ni	0	1,33	1,17	2,33	3,67	8,67
	Cr	0	0,00	0,00	0,00	0,00	0,00
	Fe	0	0,01	0,01	0,01	0,01	0,02
	Pt	0	0,12	0,02	0,05	0,07	0,12
	Pd	0	2,01	1,00	1,07	2,15	9,45

TEST 7 with 50wt% CaCl₂ addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M + 1 g/L Sn(II) Roasting time: 15 minutes Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	24.23	22.31	38.88	40.16	39.52
	Ni	0	116.25	112.72	149.36	167.68	200.07
	Cr	0	67.60	74.88	105.04	120.64	138.32
	Fe	0	806.48	775.20	871.76	919.36	973.76
	Pt	0	0.00	0.00	0.00	0.00	0.00
	Pd	0	0.00	0.00	0.01	0.01	0.04
PERCENTAGE LEACHED	Cu	0	37.50	34.54	60.19	62.17	61.18
	Ni	0	37.50	36.36	48.18	54.09	64.54
	Cr	0	0.65	0.72	1.01	1.16	1.33
	Fe	0	5.93	5.70	6.41	6.76	7.16
	Pt	0	0.00	0.02	0.00	0.09	0.15
	Pd	0	0.00	0.11	0.48	0.40	2.82

TEST 8 with 50wt% CaCl₂ addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M + 1 g/L Sn(II) Roasting time: 30 minutes Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	22.31	21.03	40.79	41.43	43.35
	Ni	0	113.43	112.72	156.40	180.36	217.00
	Cr	0	64.48	74.88	108.16	124.80	148.72
	Fe	0	816.00	799.68	927.52	964.24	1083.92
	Pt	0	0.00	0.00	0.00	0.00	0.00
	Pd	0	0.00	0.00	0.00	0.00	0.01
PERCENTAGE LEACHED	Cu	0	34.54	32.56	63.15	64.14	67.10
	Ni	0	36.59	36.36	50.45	58.18	70.00
	Cr	0	0.62	0.72	1.04	1.20	1.43
	Fe	0	6.00	5.88	6.82	7.09	7.97
	Pt	0	0.00	0.00	0.04	0.11	0.07
	Pd	0	0.00	0.00	0.00	0.00	0.51

TEST 9 with 50wt% CaCl₂ addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M + 1 g/L Sn(II) Roasting time: 60 minutes Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	32.51	28.69	29.96	33.15	29.32
	Ni	0	142.32	135.97	160.64	186.00	183.18
	Cr	0	92.56	90.48	113.36	136.24	136.24
	Fe	0	1203.60	1130.16	1313.76	1543.60	1534.08
	Pt	0	0.00	0.00	0.00	0.00	0.00
	Pd	0	0.14	0.16	0.24	0.30	0.41
PERCENTAGE LEACHED	Cu	0	50.33	44.41	46.38	51.31	45.39
	Ni	0	45.91	43.86	51.82	60.00	59.09
	Cr	0	0.89	0.87	1.09	1.31	1.31
	Fe	0	8.85	8.31	9.66	11.35	11.28
	Pt	0	0.18	0.09	0.07	0.13	0.24
	Pd	0	8.96	10.32	15.51	20.01	27.14

TEST 10 with 50wt% CaCl₂ addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M + 1 g/L Sn(II) Roasting time: 3 hours Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	21.67	21.03	16.58	22.95	22.95
	Ni	0	131.04	127.50	117.65	176.14	183.18
	Cr	0	101.92	100.88	90.48	136.24	147.68
	Fe	0	1470.16	1516.40	1406.24	2196.40	2490.16
	Pt	0	0.03	0.03	0.03	0.05	0.08
	Pd	0	0.28	0.32	0.34	0.62	0.84
PERCENTAGE LEACHED	Cu	0	33.55	32.56	25.66	35.52	35.52
	Ni	0	42.27	41.13	37.95	56.82	59.09
	Cr	0	0.98	0.97	0.87	1.31	1.42
	Fe	0	10.81	11.15	10.34	16.15	18.31
	Pt	0	2.59	2.61	2.61	3.77	5.96
	Pd	0	18.26	21.04	22.68	40.61	55.24

TEST 11 with 50wt% CaCl₂ addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M without Sn(II) Roasting time: 3 hours Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	22.95	22.31	22.95	21.67	22.95
	Ni	0	124.00	133.15	162.04	164.86	188.82
	Cr	0	98.80	102.96	120.64	121.68	143.52
	Fe	0	1313.76	1406.24	1746.24	1819.68	2279.36
	Pt	0	0.06	0.07	0.08	0.08	0.11
	Pd	0	1.37	1.33	1.40	1.30	1.43
PERCENTAGE LEACHED	Cu	0	35.52	34.54	35.52	33.55	35.52
	Ni	0	40.00	42.95	52.27	53.18	60.91
	Cr	0	0.95	0.99	1.16	1.17	1.38
	Fe	0	9.66	10.34	12.84	13.38	16.76
	Pt	0	4.82	5.13	6.62	6.53	8.64
	Pd	0	90.36	87.43	91.82	85.24	94.39

TEST 12 with 50wt% CaCl₂ addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M + 1 g/L Sn(II) Roasting time: 6 hours Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	20.40	21.03	21.03	20.40	21.03
	Ni	0	129.64	140.90	157.82	164.86	177.54
	Cr	0	97.76	105.04	118.56	124.80	137.28
	Fe	0	1470.16	1626.56	1902.64	2030.48	2370.48
	Pt	0	0.04	0.05	0.07	0.09	0.13
	Pd	0	0.34	0.41	0.58	0.80	1.18
PERCENTAGE LEACHED	Cu	0	31.58	32.56	32.56	31.58	32.56
	Ni	0	41.82	45.45	50.91	53.18	57.27
	Cr	0	0.94	1.01	1.14	1.20	1.32
	Fe	0	10.81	11.96	13.99	14.93	17.43
	Pt	0	3.33	4.01	5.79	7.02	10.26
	Pd	0	22.06	26.71	38.41	52.31	77.92

TEST 13 with 50wt% CaCl₂ and 4wt% Sn(II) addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M without Sn(II) Roasting time: 3 hours Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	28.60	27.27	28.60	29.27	29.27
	Ni	0	101.46	120.56	155.87	172.02	192.60
	Cr	0	87.36	102.96	125.84	134.16	148.72
	Fe	0	810.56	1141.04	1668.7	1946.16	2502.40
	Pt	0	0.07	0.09	0.13	0.16	0.21
	Pd	0	1.52	1.37	1.51	1.51	1.51
PERCENTAGE LEACHED	Cu	0	44.28	42.22	44.28	45.31	45.31
	Ni	0	32.73	38.89	50.28	55.49	62.13
	Cr	0	0.84	0.99	1.21	1.29	1.43
	Fe	0	5.96	8.39	12.27	14.31	18.40
	Pt	0	5.17	7.37	10.53	12.27	16.57
	Pd	0	100	90.09	99.26	99.26	99.26

TEST 14 with 50wt% CaCl₂ and 4wt% Sn(II) addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M + 1 g/L Sn(II) Roasting time: 3 hours Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	27.27	27.27	25.28	27.94	28.60
	Ni	0	124.99	138.20	141.89	172.02	194.09
	Cr	0	100.88	110.24	112.32	134.16	148.72
	Fe	0	1179.12	1361.36	1543.60	1955.68	2483.36
	Pt	0	0.03	0.03	0.04	0.07	0.12
	Pd	0	0.14	0.20	0.31	0.52	0.95
PERCENTAGE LEACHED	Cu	0	42.22	42.22	39.13	43.25	44.28
	Ni	0	40.32	44.58	45.77	55.49	62.61
	Cr	0	0.97	1.06	1.08	1.29	1.43
	Fe	0	8.67	10.01	11.35	14.38	18.26
	Pt	0	2.08	2.72	3.46	5.13	9.57
	Pd	0	9.12	13.25	20.19	33.90	62.23

TEST 15 with 50wt% CaCl₂ and 4wt% Sn(II) addition							
Mass solid: 100 g Roasting temperature: 650°C Solution volume: 1000 mL Rotational rate: 600 rpm				[HCl]: 4 M + 1 g/L I(I) Roasting time: 3 hours Leaching temperature: 95°C P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	28.60	25.94	28.60	28.60	28.60
	Ni	0	125.71	122.05	154.38	167.62	191.15
	Cr	0	105.04	104.00	126.88	134.16	146.64
	Fe	0	1198.16	1256.64	1716.32	1993.76	2530.96
	Pt	0	0.07	0.07	0.11	0.14	0.18
	Pd	0	0.92	0.58	1.11	1.24	1.43
PERCENTAGE LEACHED	Cu	0	44.28	40.16	44.28	44.28	44.28
	Ni	0	40.55	39.37	49.80	54.07	61.66
	Cr	0	1.01	1.00	1.22	1.29	1.41
	Fe	0	8.81	9.24	12.62	14.66	18.61
	Pt	0	5.58	5.63	8.92	10.57	14.00
	Pd	0	60.70	38.18	72.91	81.70	93.91

TEST 16							
Roasting stage Mass solid: 10 g Addition: 30 g CaCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	2.38	2.98	2.98	2.38	2.38
	Ni	0	21.82	21.82	21.12	23.23	25.34
	Cr	0	11.65	12.17	13.10	13.10	14.46
	Fe	0	133.69	144.70	163.06	177.07	229.16
	Pt	0	0.09	0.09	0.09	0.09	0.10
	Pd	0	0.14	0.14	0.15	0.14	0.14
PERCENTAGE LEACHED	Cu	0	36.89	46.11	46.11	36.89	36.89
	Ni	0	70.39	70.39	68.12	74.93	81.74
	Cr	0	1.12	1.17	1.26	1.26	1.39
	Fe	0	9.83	10.64	11.99	13.02	16.85
	Pt	0	72.78	74.18	73.13	72.78	75.59
	Pd	0	95.33	95.03	97.37	89.77	93.28

TEST 17							
Roasting stage Mass solid: 10 g Addition: 30 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 μm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.50	3.94	3.94	4.50	4.50
	Ni	0	26.61	25.28	28.61	29.27	27.94
	Cr	0	28.18	30.16	33.80	36.40	42.02
	Fe	0	487.29	535.84	582.35	594.86	624.10
	Pt	0	0.10	0.11	0.12	0.12	0.13
	Pd	0	0.08	0.08	0.08	0.08	0.11
PERCENTAGE LEACHED	Cu	0	69.73	61.02	61.02	69.73	69.73
	Ni	0	85.84	81.55	92.28	94.43	90.14
	Cr	0	2.71	2.90	3.25	3.50	4.04
	Fe	0	35.83	39.40	42.82	43.74	45.89
	Pt	0	78.75	86.40	94.33	95.75	98.87
	Pd	0	51.13	53.06	55.55	54.72	73.52

TEST 18							
Roasting stage Mass solid: 10 g Addition: 30 g CaCl ₂ Roasting temperature: 650°C Roasting time: 3 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 μm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	2.71	2.71	3.39	2.71	3.39
	Ni	0	16.82	20.82	23.22	24.02	23.22
	Cr	0	12.79	12.79	14.04	14.35	15.39
	Fe	0	175.44	203.05	242.35	259.08	289.95
	Pt	0	0.01	0.01	0.01	0.01	0.01
	Pd	0	0.08	0.08	0.09	0.09	0.10
PERCENTAGE LEACHED	Cu	0	41.97	41.97	52.46	41.97	52.46
	Ni	0	54.25	67.16	74.91	77.49	74.91
	Cr	0	1.23	1.23	1.35	1.38	1.48
	Fe	0	12.90	14.93	17.82	19.05	21.32
	Pt	0	7.20	7.80	9.00	8.80	9.60
	Pd	0	50.23	55.55	60.21	60.21	66.86

TEST 19							
Roasting stage Mass solid: 10 g Addition: 30 g MgCl ₂ Roasting temperature: 650°C Roasting time: 3 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.74	4.14	4.74	4.74	4.74
	Ni	0	28.68	27.28	27.28	26.58	28.68
	Cr	0	22.98	22.57	24.13	26.00	29.12
	Fe	0	432.75	452.47	483.89	494.77	502.79
	Pt	0	0.11	0.12	0.12	0.12	0.12
	Pd	0	0.06	0.07	0.08	0.09	0.10
PERCENTAGE LEACHED	Cu	0	73.31	64.15	73.31	73.31	73.31
	Ni	0	92.51	88.00	88.00	85.74	92.51
	Cr	0	2.21	2.17	2.32	2.50	2.80
	Fe	0	31.82	33.27	35.58	36.38	36.97
	Pt	0	86.29	90.83	96.07	95.73	97.12
	Pd	0	36.90	45.62	54.63	60.73	66.83

TEST 20							
Roasting stage Mass solid: 10 g Addition: 30 g AlCl ₃ Roasting temperature: 650°C Roasting time: 3 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	5.43	5.43	4.88	5.43	5.43
	Ni	0	22.43	20.51	23.07	23.72	27.56
	Cr	0	19.86	20.70	22.57	23.82	28.60
	Fe	0	327.08	339.73	364.48	373.18	395.90
	Pt	0	0.01	0.01	0.01	0.01	0.01
	Pd	0	0.13	0.13	0.13	0.15	0.14
PERCENTAGE LEACHED	Cu	0	83.98	83.98	75.58	83.98	83.98
	Ni	0	72.37	66.16	74.43	76.50	88.91
	Cr	0	1.91	1.99	2.17	2.29	2.75
	Fe	0	24.05	24.98	26.80	27.44	29.11
	Pt	0	5.60	5.92	6.08	6.72	8.32
	Pd	0	86.00	86.27	86.54	96.12	94.79

TEST 21							
Roasting stage Mass solid: 10 g Addition: 30 g AlCl ₃ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 μm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.77	4.77	4.77	5.30	4.77
	Ni	0	18.79	20.04	21.92	21.92	23.80
	Cr	0	19.55	20.80	23.09	24.44	29.54
	Fe	0	289.41	304.50	333.20	347.62	372.37
	Pt	0	0.01	0.01	0.01	0.01	0.01
	Pd	0	0.14	0.14	0.15	0.15	0.14
PERCENTAGE LEACHED	Cu	0	73.84	73.84	73.84	82.04	73.84
	Ni	0	60.60	64.64	70.70	70.70	76.76
	Cr	0	1.88	2.00	2.22	2.35	2.84
	Fe	0	21.28	22.39	24.50	25.56	27.38
	Pt	0	6.26	7.35	7.98	8.60	8.76
	Pd	0	89.75	91.83	95.73	98.07	93.91

TEST 22							
Roasting stage Mass solid: 20 g Addition: 20 g AlCl ₃ Roasting temperature: 650°C Roasting time: 3 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 μm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	9.67	9.67	9.67	9.67	9.13
	Ni	0	34.90	37.44	42.51	48.22	50.77
	Cr	0	32.66	33.07	35.36	37.44	41.81
	Fe	0	382.16	416.43	480.08	509.18	546.99
	Pt	0	0.01	0.01	0.01	0.01	0.01
	Pd	0	0.26	0.28	0.28	0.28	0.28
PERCENTAGE LEACHED	Cu	0	74.82	74.82	74.82	74.82	70.67
	Ni	0	56.29	60.38	68.57	77.78	81.88
	Cr	0	1.57	1.59	1.70	1.80	2.01
	Fe	0	14.05	15.31	17.65	18.72	20.11
	Pt	0	2.69	3.01	3.01	3.09	3.72
	Pd	0	87.12	91.08	93.05	91.60	99.38

TEST 23							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 3 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.21	5.41	5.41	5.41	4.81
	Ni	0	24.88	25.59	28.44	27.01	29.86
	Cr	0	14.35	14.77	15.50	16.02	16.64
	Fe	0	236.64	261.12	285.60	292.26	300.42
	Pt	0	0.06	0.06	0.06	0.06	0.06
	Pd	0	0.14	0.13	0.15	0.14	0.15
PERCENTAGE LEACHED	Cu	0	65.20	83.82	83.82	83.82	74.51
	Ni	0	80.26	82.55	91.73	87.14	96.31
	Cr	0	1.38	1.42	1.49	1.54	1.60
	Fe	0	17.40	19.20	21.00	21.49	22.09
	Pt	0	45.80	46.87	47.93	48.29	47.58
	Pd	0	89.48	85.94	95.68	90.66	98.34

TEST 24							
Roasting stage Mass solid: 20 g Addition: 10 g AlCl ₃ + 10 g MgCl ₂ Roasting temperature: 650°C Roasting time: 3 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	8.06	8.06	8.06	8.59	8.06
	Ni	0	41.89	44.42	48.87	47.60	49.50
	Cr	0	34.32	36.40	39.94	41.39	46.38
	Fe	0	574.74	633.76	728.42	781.46	814.64
	Pt	0	0.15	0.17	0.18	0.18	0.19
	Pd	0	0.27	0.27	0.28	0.29	0.30
PERCENTAGE LEACHED	Cu	0	62.36	62.36	62.36	66.52	62.36
	Ni	0	67.56	71.65	78.82	76.77	79.84
	Cr	0	1.65	1.75	1.92	1.99	2.23
	Fe	0	21.13	23.30	26.78	28.73	29.95
	Pt	0	58.96	65.14	71.96	69.58	74.49
	Pd	0	87.80	89.38	93.73	95.18	100

TEST 25							
Roasting stage Mass solid: 20 g Addition: 5 g AlCl ₃ + 5 g CaCl ₂ Roasting temperature: 650°C Roasting time: 3 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	7.02	7.02	7.60	7.02	7.02
	Ni	0	31.78	35.92	41.44	43.52	47.66
	Cr	0	33.28	34.32	35.57	38.69	41.81
	Fe	0	408.00	480.62	565.76	626.42	711.28
	Pt	0	0.04	0.05	0.07	0.08	0.10
	Pd	0	0.24	0.25	0.26	0.27	0.29
PERCENTAGE LEACHED	Cu	0	54.30	54.30	58.82	54.30	54.30
	Ni	0	51.25	57.93	66.84	70.19	76.87
	Cr	0	1.60	1.65	1.71	1.86	2.01
	Fe	0	15.00	17.67	20.80	23.03	26.15
	Pt	0	15.44	19.32	26.57	30.19	38.64
	Pd	0	79.77	82.07	87.09	89.38	93.97

TEST 26							
Roasting stage Mass solid: 20 g Addition: 5 g AlCl ₃ + 5 g MgCl ₂ Roasting temperature: 650°C Roasting time: 3 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	6.02	6.02	6.57	6.02	7.12
	Ni	0	36.22	39.45	43.98	45.92	45.27
	Cr	0	34.11	35.98	39.52	41.60	47.22
	Fe	0	513.54	581.81	672.11	715.36	789.62
	Pt	0	0.04	0.04	0.05	0.05	0.06
	Pd	0	0.27	0.27	0.29	0.29	0.30
PERCENTAGE LEACHED	Cu	0	46.60	46.60	50.84	46.60	55.08
	Ni	0	58.42	63.63	70.93	74.06	73.02
	Cr	0	1.64	1.73	1.90	2.00	2.27
	Fe	0	18.88	21.39	24.71	26.30	29.03
	Pt	0	15.34	16.31	18.57	20.35	22.45
	Pd	0	88.66	88.66	95.51	94.84	98.60

TEST 27							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.03	4.70	3.36	3.36	4.03
	Ni	0	16.67	23.02	25.41	26.99	26.99
	Cr	0	4.89	8.84	14.98	15.50	16.85
	Fe	0	57.94	106.90	397.66	429.08	455.60
	Pt	0	0.03	0.04	0.11	0.11	0.11
	Pd	0	0.10	0.13	0.13	0.13	0.13
PERCENTAGE LEACHED	Cu	0	62.41	72.81	52.01	52.01	62.41
	Ni	0	53.78	74.27	81.96	87.08	87.08
	Cr	0	0.47	0.85	1.44	1.49	1.62
	Fe	0	4.26	7.86	29.24	31.55	33.50
	Pt	0	23.79	31.72	87.24	87.24	87.24
	Pd	0	65.96	82.46	82.46	82.46	82.46

TEST 28							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.27	3.27	3.92	3.92	3.92
	Ni	0	22.40	22.40	25.49	25.49	27.81
	Cr	0	10.09	11.02	13.62	15.39	16.85
	Fe	0	217.60	282.06	397.39	459.41	524.69
	Pt	0	0.05	0.07	0.10	0.12	0.13
	Pd	0	0.12	0.12	0.12	0.12	0.12
PERCENTAGE LEACHED	Cu	0	50.61	50.61	60.73	60.73	60.73
	Ni	0	72.27	72.27	82.24	82.24	89.71
	Cr	0	0.97	1.06	1.31	1.48	1.62
	Fe	0	16.00	20.74	29.22	33.78	38.58
	Pt	0	38.59	54.02	77.17	92.61	99.94
	Pd	0	80.23	80.23	80.23	80.23	80.23

TEST 29							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 1 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 μm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.38	3.38	4.06	4.06	3.38
	Ni	0	21.57	20.77	21.57	23.96	24.76
	Cr	0	9.36	10.19	11.23	14.35	14.35
	Fe	0	131.65	151.64	202.50	322.59	322.59
	Pt	0	0.04	0.04	0.05	0.09	0.09
	Pd	0	0.10	0.10	0.10	0.13	0.13
PERCENTAGE LEACHED	Cu	0	52.33	52.33	62.79	62.79	52.33
	Ni	0	69.57	67.00	69.57	77.30	79.88
	Cr	0	0.90	0.98	1.08	1.38	1.38
	Fe	0	9.68	11.15	14.89	23.72	23.72
	Pt	0	31.92	31.92	39.90	71.82	71.82
	Pd	0	66.37	66.37	66.37	82.96	82.96

TEST 30							
Roasting stage Mass solid: 20 g Addition: 10 g CaCl ₂ + 10 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 μm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.23	3.23	3.23	3.88	3.88
	Ni	0	34.37	38.95	44.30	47.35	47.35
	Cr	0	23.30	26.62	30.37	32.24	35.57
	Fe	0	574.46	695.78	836.67	900.59	972.13
	Pt	0	0.11	0.14	0.16	0.17	0.19
	Pd	0	0.29	0.27	0.29	0.29	0.30
PERCENTAGE LEACHED	Cu	0	25.02	25.02	25.02	30.02	30.02
	Ni	0	55.43	62.82	71.45	76.37	76.37
	Cr	0	1.12	1.28	1.46	1.55	1.71
	Fe	0	21.12	25.58	30.76	33.11	35.74
	Pt	0	41.96	53.41	61.04	64.85	72.48
	Pd	0	95.18	87.25	95.18	95.18	99.94

TEST 31							
Roasting stage Mass solid: 20 g Addition: 10 g CaCl ₂ + 10 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	6.26	6.26	6.26	6.26	6.26
	Ni	0	36.97	39.93	46.59	50.28	51.76
	Cr	0	24.13	25.79	28.50	32.03	31.62
	Fe	0	390.32	483.89	640.29	802.40	794.78
	Pt	0	0.09	0.11	0.14	0.17	0.18
	Pd	0	0.26	0.28	0.28	0.26	0.28
PERCENTAGE LEACHED	Cu	0	48.44	48.44	48.44	48.44	48.44
	Ni	0	59.63	64.40	75.14	81.10	83.49
	Cr	0	1.16	1.24	1.37	1.54	1.52
	Fe	0	14.35	17.79	23.54	29.50	29.22
	Pt	0	36.93	44.32	55.40	66.48	70.17
	Pd	0	84.48	92.15	92.15	84.48	92.15

TEST 32							
Roasting stage Mass solid: 20 g Addition: 10 g CaCl ₂ + 10 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 1 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.64	3.64	3.64	3.03	2.43
	Ni	0	20.79	20.79	22.94	24.37	25.81
	Cr	0	16.85	17.47	19.55	20.80	23.71
	Fe	0	181.70	200.46	241.54	271.46	317.97
	Pt	0	0.02	0.03	0.03	0.04	0.05
	Pd	0	0.27	0.27	0.27	0.27	0.27
PERCENTAGE LEACHED	Cu	0	28.18	28.18	28.18	23.48	18.78
	Ni	0	33.53	33.53	37.00	39.31	41.63
	Cr	0	0.81	0.84	0.94	1.00	1.14
	Fe	0	6.68	7.37	8.88	9.98	11.69
	Pt	0	7.16	10.74	10.74	14.32	17.90
	Pd	0	89.34	89.34	89.34	89.34	89.34

TEST 33							
Roasting stage Mass solid: 20 g Addition: 5 g CaCl ₂ + 5 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.62	4.62	4.62	4.62	4.62
	Ni	0	39.53	43.62	49.07	49.07	49.07
	Cr	0	32.03	32.86	35.15	35.98	39.52
	Fe	0	551.89	639.20	732.50	767.86	832.05
	Pt	0	0.04	0.06	0.06	0.07	0.09
	Pd	0	0.26	0.28	0.28	0.28	0.30
PERCENTAGE LEACHED	Cu	0	35.72	35.72	35.72	35.72	35.72
	Ni	0	63.75	70.35	79.14	79.14	79.14
	Cr	0	1.54	1.58	1.69	1.73	1.90
	Fe	0	20.29	23.50	26.93	28.23	30.59
	Pt	0	17.02	23.83	23.83	27.23	34.04
	Pd	0	84.93	92.01	92.01	92.01	99.09

TEST 34							
Roasting stage Mass solid: 20 g Addition: 5 g CaCl ₂ + 5 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	2.47	3.08	3.08	3.08	3.08
	Ni	0	27.66	32.03	40.77	42.95	45.14
	Cr	0	24.34	26.00	28.50	29.33	32.66
	Fe	0	347.89	431.39	569.57	625.06	719.98
	Pt	0	0.02	0.04	0.05	0.06	0.07
	Pd	0	0.23	0.28	0.25	0.28	0.28
PERCENTAGE LEACHED	Cu	0	19.08	23.84	23.84	23.84	23.84
	Ni	0	44.62	51.66	65.75	69.28	72.80
	Cr	0	1.17	1.25	1.37	1.41	1.57
	Fe	0	12.79	15.86	20.94	22.98	26.47
	Pt	0	7.27	14.54	18.18	21.82	25.45
	Pd	0	75.61	90.73	83.17	90.73	90.73

TEST 35							
Roasting stage Mass solid: 20 g Addition: 5 g CaCl ₂ + 5 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 1 M Leaching temperature: 95°C Rotational rate: 600 rpm P ₈₀ = 16 μm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.48	3.48	3.48	4.06	4.06
	Ni	0	22.64	22.64	24.69	25.38	28.12
	Cr	0	27.04	27.87	29.95	30.58	32.66
	Fe	0	221.14	234.74	268.46	288.32	337.01
	Pt	0	0.00	0.01	0.02	0.02	0.03
	Pd	0	0.15	0.15	0.17	0.19	0.26
PERCENTAGE LEACHED	Cu	0	26.96	26.96	26.96	31.45	31.45
	Ni	0	36.51	36.51	39.83	40.93	45.36
	Cr	0	1.30	1.34	1.44	1.47	1.57
	Fe	0	8.13	8.63	9.87	10.60	12.39
	Pt	0	0.00	3.43	6.85	6.85	10.28
	Pd	0	49.86	49.86	56.99	64.11	85.48

TEST 36							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 25°C Rotational rate: 600 rpm P ₈₀ = 30 μm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.98	4.47	4.47	4.47	4.47
	Ni	0	21.72	22.90	23.49	22.31	24.07
	Cr	0	5.72	6.55	7.07	7.07	7.80
	Fe	0	76.57	84.59	88.26	91.26	106.62
	Pt	0	0.05	0.05	0.06	0.06	0.07
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	61.54	69.23	69.23	69.23	69.23
	Ni	0	70.08	73.86	75.76	71.97	77.65
	Cr	0	0.55	0.63	0.68	0.68	0.75
	Fe	0	5.63	6.22	6.49	6.71	7.84
	Pt	0	35.48	40.18	46.63	46.63	51.91
	Pd	0	98.54	100.00	100.00	100.00	100.00

TEST 37							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 50°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.98	3.98	3.98	3.98	3.98
	Ni	0	19.96	19.96	21.14	22.90	22.90
	Cr	0	4.58	4.99	5.30	5.72	7.80
	Fe	0	98.06	113.97	140.35	170.95	292.81
	Pt	0	0.04	0.04	0.05	0.06	0.09
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	61.54	61.54	61.54	61.54	61.54
	Ni	0	64.39	64.39	68.18	73.86	73.86
	Cr	0	0.44	0.48	0.51	0.55	0.75
	Fe	0	7.21	8.38	10.32	12.57	21.53
	Pt	0	31.38	32.84	40.18	46.04	72.14
	Pd	0	100.00	100.00	100.00	100.00	100.00

TEST 38							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 75°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.98	3.98	3.48	3.98	3.98
	Ni	0	21.72	22.31	22.90	24.07	26.42
	Cr	0	5.72	6.34	8.22	9.98	13.73
	Fe	0	132.87	183.19	297.16	372.50	498.71
	Pt	0	0.06	0.06	0.09	0.11	0.13
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	61.54	61.54	53.85	61.54	61.54
	Ni	0	70.08	71.97	73.86	77.65	85.23
	Cr	0	0.55	0.61	0.79	0.96	1.32
	Fe	0	9.77	13.47	21.85	27.39	36.67
	Pt	0	44.28	49.27	69.21	87.68	99.71
	Pd	0	100.00	100.00	100.00	100.00	100.00

TEST 39							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 90°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.97	4.97	4.47	4.47	4.47
	Ni	0	25.25	25.25	26.42	27.01	26.42
	Cr	0	9.36	9.36	10.09	11.13	11.44
	Fe	0	204.68	204.68	266.42	338.10	349.25
	Pt	0	0.10	0.10	0.11	0.13	0.13
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	76.92	76.92	69.23	69.23	69.23
	Ni	0	81.44	81.44	85.23	87.12	85.23
	Cr	0	0.90	0.90	0.97	1.07	1.10
	Fe	0	15.05	15.05	19.59	24.86	25.68
	Pt	0	75.37	75.37	86.22	99.71	99.71
	Pd	0	100.00	100.00	100.00	100.00	100.00

TEST 40							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 90°C Rotational rate: 140 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.47	4.47	4.47	4.97	4.97
	Ni	0	25.83	25.83	25.83	27.01	28.18
	Cr	0	8.42	8.94	10.30	10.92	13.00
	Fe	0	179.52	227.94	291.58	315.52	362.03
	Pt	0	0.09	0.11	0.12	0.13	0.13
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	69.23	69.23	69.23	76.92	76.92
	Ni	0	83.33	83.33	83.33	87.12	90.91
	Cr	0	0.81	0.86	0.99	1.05	1.25
	Fe	0	13.20	16.76	21.44	23.20	26.62
	Pt	0	71.85	82.70	92.08	100.00	100.00
	Pd	0	100.00	100.00	100.00	100.00	100.00

TEST 41							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 90°C Rotational rate: 280 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.48	3.48	3.48	3.98	3.98
	Ni	0	17.61	21.14	24.07	25.25	27.01
	Cr	0	6.34	7.80	10.92	12.38	15.08
	Fe	0	199.10	282.47	428.26	499.94	581.94
	Pt	0	0.07	0.09	0.12	0.13	0.13
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	53.85	53.85	53.85	61.54	61.54
	Ni	0	56.82	68.18	77.65	81.44	87.12
	Cr	0	0.61	0.75	1.05	1.19	1.45
	Fe	0	14.64	20.77	31.49	36.76	42.79
	Pt	0	52.20	67.16	94.43	99.71	99.71
	Pd	0	100.00	100.00	100.00	100.00	100.00

TEST 42							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 90°C Rotational rate: 420 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.48	3.48	3.98	3.98	3.98
	Ni	0	21.72	22.90	25.25	25.83	27.60
	Cr	0	6.66	8.01	10.92	13.00	15.29
	Fe	0	252.96	330.21	455.74	521.97	605.88
	Pt	0	0.08	0.10	0.13	0.13	0.13
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	53.85	53.85	61.54	61.54	61.54
	Ni	0	70.08	73.86	81.44	83.33	89.02
	Cr	0	0.64	0.77	1.05	1.25	1.47
	Fe	0	18.60	24.28	33.51	38.38	44.55
	Pt	0	65.69	79.47	100.00	100.00	100.00
	Pd	0	100.00	100.00	100.00	100.00	100.00

TEST 43							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 90°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	4.97	4.47	4.47	4.47	4.47
	Ni	0	25.25	26.42	27.01	26.42	27.01
	Cr	0	9.36	10.09	11.13	11.44	11.65
	Fe	0	204.68	266.42	338.10	349.25	367.61
	Pt	0	0.10	0.11	0.13	0.13	0.13
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	76.92	69.23	69.23	69.23	69.23
	Ni	0	81.44	85.23	87.12	85.23	87.12
	Cr	0	0.90	0.97	1.07	1.10	1.12
	Fe	0	15.05	19.59	24.86	25.68	27.03
	Pt	0	75.37	86.22	99.71	99.71	99.71
	Pd	0	100.00	100.00	100.00	100.00	100.00

TEST 44							
Roasting stage Mass solid: 250 g Addition: 375 g CaCl ₂ + 375 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 3 M Leaching temperature: 90°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	12.42	0.00	0.00	0.00	0.00
	Ni	0	0.00	0.00	0.00	0.00	0.00
	Cr	0	72.80	72.80	46.80	44.20	39.00
	Fe	0	6.80	0.00	0.00	0.00	0.00
	Pt	0	0.35	0.40	0.23	0.17	0.14
	Pd	0	3.80	3.80	3.80	3.80	3.80
PERCENTAGE LEACHED	Cu	0	7.69	0.00	0.00	0.00	0.00
	Ni	0	0.00	0.00	0.00	0.00	0.00
	Cr	0	0.28	0.28	0.18	0.17	0.15
	Fe	0	0.02	0.00	0.00	0.00	0.00
	Pt	0	11.00	12.61	7.04	5.43	4.40
	Pd	0	100.00	100.00	100.00	100.00	100.00

TEST 45							
Roasting stage Mass solid: 10 g Addition: 15 g CaCl ₂ + 15 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 90°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	3.98	3.98	3.48	3.98	3.98
	Ni	0	27.60	27.60	28.18	29.36	29.36
	Cr	0	12.38	13.21	14.14	14.77	15.08
	Fe	0	322.86	388.96	441.73	451.52	463.08
	Pt	0	0.09	0.11	0.13	0.13	0.13
	Pd	0	0.15	0.15	0.15	0.15	0.15
PERCENTAGE LEACHED	Cu	0	61.54	61.54	53.85	61.54	61.54
	Ni	0	89.02	89.02	90.91	94.70	94.70
	Cr	0	1.19	1.27	1.36	1.42	1.45
	Fe	0	23.74	28.60	32.48	33.20	34.05
	Pt	0	73.31	87.98	99.71	99.71	99.71
	Pd	0	100	100	100	100	100

TEST 46							
Roasting stage Mass solid: 50 g Addition: 75 g CaCl ₂ + 75 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 90°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	23.36	23.36	24.35	24.35	24.35
	Ni	0	126.82	131.52	133.86	136.21	140.91
	Cr	0	59.28	60.84	68.12	70.20	75.92
	Fe	0	1390.60	1574.20	1887.00	1966.56	2095.08
	Pt	0	0.53	0.60	0.64	0.64	0.64
	Pd	0	0.76	0.76	0.76	0.76	0.76
PERCENTAGE LEACHED	Cu	0	72.31	72.31	75.38	75.38	75.38
	Ni	0	81.82	84.85	86.36	87.88	90.91
	Cr	0	1.14	1.17	1.31	1.35	1.46
	Fe	0	20.45	23.15	27.75	28.92	30.81
	Pt	0	82.11	93.84	99.71	99.71	99.71
	Pd	0	100	100	100	100	100

TEST 47							
Roasting stage Mass solid: 250 g Addition: 375 g CaCl ₂ + 375 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 90°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	24.84	19.88	11.92	5.96	1.49
	Ni	0	1.16	0.62	0.62	1.16	0.62
	Cr	0	0.00	0.00	0.00	0.00	0.00
	Fe	0	0.00	0.00	0.00	0.00	0.00
	Pt	0	0.04	0.00	0.00	0.00	0.00
	Pd	0	0.47	0.39	0.19	0.10	0.09
PERCENTAGE LEACHED	Cu	0	15.38	12.31	7.38	3.69	0.92
	Ni	0	0.15	0.08	0.08	0.15	0.08
	Cr	0	0.00	0.00	0.00	0.00	0.00
	Fe	0	0.00	0.00	0.00	0.00	0.00
	Pt	0	1.17	0.00	0.00	0.00	0.00
	Pd	0	12.29	10.15	5.07	2.73	2.34

TEST 48							
Roasting stage Mass solid: 100 g Addition: 300 g CaCl ₂ + 300 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 90°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	42.73	41.74	41.25	42.24	52.67
	Ni	0	217.25	221.93	218.40	225.46	281.82
	Cr	0	66.56	62.40	56.16	56.16	62.40
	Fe	0	673.20	568.48	386.24	293.76	141.44
	Pt	0	0.53	0.54	0.53	0.56	0.79
	Pd	0	1.49	1.52	1.52	1.52	1.52
PERCENTAGE LEACHED	Cu	0	66.15	64.62	63.85	65.38	81.54
	Ni	0	70.08	71.59	70.45	72.73	90.91
	Cr	0	0.64	0.60	0.54	0.54	0.60
	Fe	0	4.95	4.18	2.84	2.16	1.04
	Pt	0	41.06	42.52	41.06	43.99	61.58
	Pd	0	98.05	100	100	100	100

TEST 49							
Roasting stage Mass solid: 100 g Addition: 300 g CaCl ₂ + 300 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 70°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	36.77	36.27	38.26	37.27	39.75
	Ni	0	179.65	179.65	185.54	178.50	189.04
	Cr	0	58.24	58.24	63.44	63.44	70.72
	Fe	0	1255.28	1279.76	1335.52	1304.24	1360.00
	Pt	0	0.39	0.39	0.43	0.43	0.45
	Pd	0	1.47	1.47	1.46	1.45	1.46
PERCENTAGE LEACHED	Cu	0	56.92	56.15	59.23	57.69	61.54
	Ni	0	57.95	57.95	59.85	57.58	60.98
	Cr	0	0.56	0.56	0.61	0.61	0.68
	Fe	0	9.23	9.41	9.82	9.59	10.00
	Pt	0	30.79	30.79	33.72	33.72	35.19
	Pd	0	96.59	96.59	96.10	95.12	96.10

TEST 50							
Roasting stage Mass solid: 50 g Addition: 150 g CaCl ₂ + 150 g MgCl ₂ Roasting temperature: 650°C Roasting time: 6 hours				Leaching stage [HCl]: 6 M Leaching temperature: 70°C Rotational rate: 600 rpm P ₈₀ = 30 µm			
Leaching time (hour)		0	0.5	1	3	6	24
LEACHATE (ppm)	Cu	0	20.37	21.37	20.87	20.87	21.37
	Ni	0	109.20	112.73	115.66	114.48	122.12
	Cr	0	42.64	46.80	50.96	53.56	59.28
	Fe	0	784.04	1004.36	1396.72	1635.40	1935.96
	Pt	0	0.38	0.45	0.51	0.60	0.64
	Pd	0	0.73	0.75	0.73	0.72	0.75
PERCENTAGE LEACHED	Cu	0	63.08	66.15	64.62	64.62	66.15
	Ni	0	70.45	72.73	74.62	73.86	78.79
	Cr	0	0.82	0.90	0.98	1.03	1.14
	Fe	0	11.53	14.77	20.54	24.05	28.47
	Pt	0	58.65	70.38	79.18	93.84	99.71
	Pd	0	96.59	98.54	96.59	94.63	98.54

BIBLIOGRAPHY

The following comprehensive bibliographical section lists all references cited in all papers representing the body of research of this PhD thesis.

BIBLIOGRAPHY

Adams, M., Lawrence, R., Bratty, M., 2008. Biogenic sulfide for cyanide recycle and copper recovery in gold-copper ore processing. *Minerals Engineering* 21(6), 509–517.

Adams, M., Liddell, K., Holohan, T., 2011. Hydrometallurgical processing of Platreef flotation concentrate. *Minerals Engineering* 24, 545–550.

Adams, M.D., 2005. *Advances in Gold Ore Processing*, first ed. Wills, B.A., Netherlands.

Adams, M.D., McDougall, G.J., Hancock, R.D., 1987. Models for the adsorption of aurocyanide onto activated carbon. Part III: Comparison between the extraction of aurocyanide by activated carbon, Polymeric adsorbents and 1-Pentanol. *Hydrometallurgy* 19, 95-115.

Afenya, P.M., 1991. Treatment of carbonaceous refractory gold ores. *Minerals Engineering* 4(7–11), 1043–1055.

Afolabi, A.S., Nkobane, M.P., Abdulkareem, A.S., 2012. Development of PGMs and chrome extraction circuit from UG-2 ore. In: *Proceedings of the World Congress on Engineering*, vol. 3.

Aguilar, M., Farran, A., Marti, V., 1997. Capillary electrophoretic determination of cyanide leaching solutions from automobile catalytic converters. *Journal of chromatography A* 778, 397–402.

Al-Bazi, S.J., Chow, A., 1984. Platinum metals-solution chemistry and separation methods (ion exchange and solvent extraction). *Talanta* 31(10A), 815-836.

Anderson, C.G., 2003. Treatment of copper ores and concentrates with industrial nitrogen species catalyzed pressure leaching and non-cyanide precious metals recovery. *The Journal of The Minerals, Metals and Materials Society (TMS)* 55, 32–36.

AngloAmerican, 2011. *Building the Foundations for a Future through Mining. Integrated Annual Report, 2011.*

Antony, M.P., Tathavadkar, V.D., Calvert, C.C., Jha, A., 2001. The soda-ash roasting of chromite ore processing residue for the reclamation of chromium. *Metallurgical and Materials Transactions B* 32(6), 987–995.

Asamoah-Bekoe, Y., 1998. Investigation of the leaching of the platinum-group metal concentrate in hydrochloric acid solution by chlorine. MSc Thesis, University of the Witwatersrand, South Africa.

Assis, S., Montenegro, L., Peres, A., 1996. Utilisation of hydroxamates in minerals froth flotation. *Minerals Engineering* 9(1), 103-114.

- Awadalla, F.T., Molnar, R.E., Riteey, G.M., 1994. U.S. Patent N° 5,304,233. Washington, DC: U.S. Patent and Trademark Office.
- Aylmore, M.G., 2005. Alternative lixivants to cyanide for leaching gold ores. *Developments in Mineral Processing* 15, 501–539.
- Azaroual, M., Romand, B., Freyssinet, P., Disnar, J.R., 2001. Solubility of platinum in aqueous solutions at 25°C and pHs 4 to 10 under oxidizing conditions. *Geochimica and Cosmochimica Acta* 65(24), 4453–4466.
- Azharul, I.M., Sakkas, V., Triantafyllos, A.A., 2009. Application of statistical design of experiment with desirability functions for the removal of organophosphorus pesticide from aqueous solution by low-cost material. *Journal of Hazardous Materials* 170(1), 230–238.
- Baghalha, M., 2012. The leaching kinetics of an oxide gold ore with iodide/iodine solutions. *Hydrometallurgy* 113–114, 42–50.
- Baglin, E.G., Gomes, J.M., Carnahan, T.G., Snider, J.M., 1985. Recovery of platinum, palladium, and gold from Stillwater Complex flotation concentrate by a roasting-leaching procedure. *Complex Sulfides-Processing of ores, concentrates and by-products*, San Diego, California, 10-13.
- Bahamòndez, C., Castro, R., Vargas, T., Arancibia, E., 2016. In situ mining through leaching: experimental methodology for evaluating its implementation and economic considerations. *Journal of the South African Institute of Mining and Metallurgy* 116(7), 689–698.
- Bai, L., Barnes, S.J., Baker, D.R., 2017. Sperrylite saturation in magmatic sulfide melts: Implications for formation of PGE-bearing arsenides and sulfarsenides. *American Mineralogist* 102(5), 966-974.
- Baimbetov, B.S., Aitenov, K.D., Bekisheva, A.A., Abdikerim B.E., 2015. Metallic sulphide and sodium carbonate interacting processes. *Metallurgical and Mining Industry* (11).
- Balaz, P., Boldizarova, E., Achimovicova, M., Kammel, R., 2000. Leaching and dissolution of a pentlandite concentrate pretreated by mechanical activation. *Hydrometallurgy* 57, 85–96.
- Basturkcu, H., Acarkan, N., 2016. Separation of nickel and iron from lateritic ore using a digestion–roasting–leaching–precipitation process. *Physicochemical Problems of Mineral Processing* 52(2), 564–574.
- Bax, A., 2004. Recovery of Platinum Group Metals. AP/P/2005/003433, Appl. 08/04/2004, Acc. 12/12/2008.
- Bax, A., Dunn, G.M., Lewins, D., 2009. Recovery of Platinum Group Metals. USA Patent 7,544,231 B2.

- Becker, M., Wiese, J., Ramonotsi, M., 2014. Investigation into the mineralogy and flotation performance of oxidised PGM ore. *Minerals Engineering* 65, 24-32.
- Benke, G., Gnot, W., 2002. The electrochemical dissolution of platinum. *Hydrometallurgy* 64, 205-218.
- Bernardis, F.L., Grant, R.A., Sherrington, D.C., 2005. A review of methods of separation of the platinum-group metals through their chloro-complexes. *Reactive and functional polymers* 65(3), 205-217.
- Bezuidenhout, G.A., Davis, J., van Beek, B., Eksteen, J.J., 2012. Operation of a concentrated mode dual-alkali scrubber plant at the Lonmin smelter. *The Journal of the Southern African Institute of Mining and Metallurgy* 112(7), 657–665.
- Botz, M.M., Dimitriadis, D., Polglase, T., Phillips, W., Jenny, R., 2001. Processes for the regeneration of cyanide from thiocyanate. *Minerals and Metallurgical Processing* 18(3).
- Braemore resources Plc., 2009. Annual Report & Consolidated Financial Statements for the Year Ended 30 June 2009.
- Breuer, P.L., Hewitt, D.M., Sutcliffe, C.A., Jeffrey, M.I., 2009. The quantification of cyanide and its reaction products during leaching and cyanide destruction processes. In: *World Gold 2009 Conference*. The Southern African Institute of Mining and Metallurgy, Johannesburg, pp. 287–294.
- Brierley, J.A., Brierley, C.L., 2001. Present and future commercial applications of biohydrometallurgy. *Hydrometallurgy* 59(2), 233–239.
- Broadhurst, J.L., Du Perez, J.G.H., 1993. A thermodynamic study of the dissolution of gold in an acidic aqueous thiocyanate medium using iron (III) sulphate as an oxidant. *Hydrometallurgy* 32(3), 317-344.
- Bulatovic, S., 2003. Evaluation of alternative reagent schemes for the flotation of platinum group minerals from various ores. *Minerals Engineering* 16(10), 931-939.
- Carneiro, M.F.C., Leão, V.A., 2007. The role of sodium chloride on surface properties of chalcopyrite leached with ferric sulfate. *Hydrometallurgy* 87, 73–82.
- Chen, J., Huang, K., 2006. A new technique for extraction of platinum group metals by pressure cyanidation. *Hydrometallurgy* 82, 164–171.
- Chou, E.C.J., 1986. Production of high surface area nickel powder. United States Patent 4,758,266.
- Chowdhury, Z.Z., Zain, S.M., Khan, R.A., Ahmad, A.A., Khalid, K., 2012. Application of response surface methodology (RSM) for optimizing production condition for removal of Pb(II) and Cu(II) onto Kenaf fiber based activated carbon. *Research Journal of Applied Sciences Engineering and Technology* 4(5), 458–465.

Chusova, T.P., Semenova, Z.I., 2008. Thermodynamics of the Pt-Cl system. *Thermochimica Acta* 469(1), 59-64.

Cole, S., Joe Ferron, C., 2002. A Review of the Beneficiation and Extractive Metallurgy of the Platinum Group Elements, Highlighting Recent Process Innovations. SGS Minerals Services Technical Paper 2002-03.

Córdoba, E.M., Muñoz, J.A., Blázquez, M.L., González, F., Ballester, A., 2008. Leaching of chalcopyrite with ferric ion. Part III: effect of redox potential on the silvercatalyzed process. *Hydrometallurgy* 93, 97–105.

Cramer, L. A., 2001. The extractive metallurgy of South Africa's platinum ores. *The Journal of The Minerals, Metals & Materials Society (TMS)* 53(10), 14-18.

Crundwell, F.K., 2013. The dissolution and leaching of minerals: mechanisms, myths and misunderstandings. *Hydrometallurgy* 139, 132-148.

Crundwell, F.K., Moats, M., Ramachandran, V., 2011. Extractive metallurgy of nickel, cobalt and platinum group metals. Elsevier.

Cyanide management, 2008. Department of Resources, Energy and Tourism. Australian Government.

Dabrowski, A., 2001. Adsorption-from theory to practice. *Advances in Colloid and Interface Science* 93, 135-224.

Dadgar, A., Howarth, J.N., Sergent, R.H., Favstritsky, N.A., McKeown, J.A., Borden, D.W., Sanders, B.M., Likens, J., 1997. Inorganic Perbromide Compositions and Methods of Use Thereof. United States Patent Number 5,607,619.

Davidson, R.J., Schmidt, C.G., 1986. A review of the AARL process for the elution of gold from activated carbon. In 13th CMMI Congress 4, 215-225.

Dawson, R.J., Kelsall, G.H., 2007. Recovery of platinum group metals from secondary materials. I. Palladium dissolution in iodide solutions. *Journal of applied electrochemistry* 37(1), 3-14.

Debemardi, G., Gentina, J.C., Albistur, P., Slanzi, G., 2013. Evaluation of processing options to avoid the passivation of chalcopyrite. *International Journal of Mineral Processing* 125, 1-4.

Demopoulos, G.P., 1989. Refining of platinum-group metals. *Canadian Mining and Metallurgical Bulletin* 82(923), 165-171.

Deschenes, G., 2005. Advances in the cyanidation of gold. *Developments in Mineral Processing* 15, 479–500.

Dimitrijevic, M.D., Urosevic, D.M., Jankovic, Z.D., Milic, S.M., 2016. Recovery of copper from smelting slag by sulphation roasting and water leaching. *Physicochemical Problems of Mineral Processing* 52(1).

Dixon, D.G., Tshilombo, A.F., 2005. Leaching Process for Copper Concentrates. United States Patent Application 2005/0269208 A1.

Doná, E., Cordin, M., Deisl, C., Bertel, E., Franchini, C., Zucca, R., Redinger, J., 2009. Halogen-induced corrosion of platinum. *Journal of the American Chemical Society* 131(8), 2827-2829.

Dreisinger, D., 2006. Copper leaching from primary sulfides: options for biological and chemical extraction of copper. *Hydrometallurgy* 83, 10–20.

Dreisinger, D., 2012. Hydrometallurgical extraction of base, rare, and precious metals from complex and low grade resources. In: XXVI International Mineral Processing Congress (IMPC) 2012 Proceedings/New Delhi, India/24–28 September 2012.

Dubrovsky, M., 1991. U.S. Patent N° 5,074,910. Washington, DC: U.S. Patent and Trademark Office.

Dumeignil, F., Amano, H., Wang, D., Qian, E.W., Ishihara, A., Kabe, T., 2003. Study of the sulfidation process of $\text{CrO}_3\text{-Al}_2\text{O}_3$ hydrodesulfurization catalysts by a ^{35}S -labeled H_2S pulse tracer method. *Applied Catalysis A* 249(2), 255–263.

Dunn, J.G., Ibrado, A.S., Graham, J., 1995. Pyrolysis of arsenopyrite for gold recovery by cyanidation. *Minerals Engineering* 8(4), 459-471.

Dunne, R., Levier, M., Acar, S., Kappes, R., 2009. Keynote address: Newmont's contribution to gold technology. In: World Gold Conference 2009, The Southern African Institute of Mining and Metallurgy.

Dutrizac, J.E., 1983. Factors affecting alkali jarosite precipitation. *Metallurgical Transactions B* 14(4), 531-539.

Dyosi, Z., McCrindle, R.I., Wondimu, T., Botha, B.M., Ndibewu, P.P., 2009. The use of Dowex-M43 ion exchange resin in the determination of Pt and Pd in converter matte by ICP-OES. *South African Journal of Chemistry* 62, 5-5.

Eksteen, J.J., 2011. A mechanistic model to predict matte temperatures during the smelting of UG2-rich blends of Platinum Group Metal concentrate. *Minerals Engineering* 24(7), 676–687.

Eksteen, J.J., Bezuidenhout, G.A., van Beek, B., 2011. Cracking a hard nut: an overview of Lonmin's operations directed at smelting of UG2-rich concentrate blends. *Journal of the South African Institute of Mining and Metallurgy* 111(10), 681–690.

Eksteen, J.J., Onyango, M.S., Pelsler, M., Lorenzen, L., Aldrich, C., Georgalli, G.A., 2008. Effects of residence time and mixing regimes on the precipitation characteristics of CaF_2 and MgF_2 from high ionic strength sulfate solutions. *Hydrometallurgy* 91(1–4), 104–112.

- Elding, L.I., 1978. Stabilities of platinum(II) chloro and bromo complexes and kinetics for anation of the tetraaquaplatinum(II) ion by halides and thiocyanate. *Inorganica Chimica Acta* 28, 255–262.
- Ellis, S., 2003. Ultra Fine Grinding-a Practical Alternative to Oxidative Treatment of Refractory Gold Ores. Townsville: Queensland, pp. 11–17.
- Ellis, S., Mines, K.C.G., Kalgoorlie, W.A., 2008. Ultra Fine Grinding – A Practical Alternative to Oxidative Treatment of Refractory Gold Ores.
- Epstein, I.R., Kustin, K., Warshaw, L.J., 1980. A kinetics study of the oxidation of iron(II) by nitric acid. *Journal of the American Chemical Society* 102(11), 3751–3758.
- Evans, D.M., 2002. Potential for bulk mining of oxidized platinum-group element deposits. *Applied Earth Science* 111(1), 81-86.
- Fact Sheet., 2012. Platinum Group Metals. Polinares Working Paper 35 March 2012.
- Farinha, P.A., Correia, M.J.N., Carvalho, J.R., 1992. Technical note leaching of gold from a Portuguese concentrate with thiourea. *Minerals Engineering* 5(8), 953–959.
- Ferron, C.J., Hamilton, C.C., Valeyev, O., McKay, N., 2006. The Effect of the Mineralogy of the Platinum Group Metals on their Leachability During the Platsol® Leach Process. SGS Minerals Services Technical Paper, 3.
- Flatman, S., Battersby, R.M., Imhof, R., Battersby, R.M., Ibrayev, S., 2010. The Leachox™ refractory gold process – the setting, design, installation and commissioning of a large scale plant at the Vasgold gold mine, Kazakhstan. *Precious Metals* 10.
- Fleming, C.A., 1992. Hydrometallurgy of precious metals recovery. *Hydrometallurgy* 30, 127–162.
- Fleming, C.A., 2002. Platsol™ Process Provides a Viable Alternative to Smelting. SGS Minerals Services Technical Paper 2002-01.
- Fleming, C.A., Cromberge, G., 1984. The extraction of gold from cyanide solutions by strong-and weak-base anion exchange resins. *Journal of the Southern African Institute of Mining and Metallurgy* 84(5), 125-137.
- Fleming, C.A., Nicol, M.J., 1984. The absorption of gold cyanide onto activated carbon. III. Factors Influencing the Rate of Loading and the Equilibrium Capacity. *Journal of the Southern African Institute of Mining and Metallurgy* 84(4), 85-93.
- Fontàs, C., Hidalgo, M., Salvadó, V., 2009. Adsorption and Preconcentration of Pd(II), Pt(IV), and Rh(III) using Anion-Exchange Solid-Phase Extraction Cartridges (SPE). *Solvent Extraction and Ion Exchange* 27(1), 83-96.

Frankiewicz, T.C., 1978. U.S. Patent N° 4,110,106. U.S. Patent and Trademark Office, Washington DC, United States of America.

Fursman, O.C., 1962. Recovery of Mineral Values in Cupriferous and Nickeliferous Pyrrhotite. US Department of the Interior, Bureau of Mines.

Gaita, R., Al-Bazi, S.J., 1995. An ion-exchange method for selective separation of palladium, platinum and rhodium from solutions obtained by leaching automotive catalytic converters. *Talanta* 42(2), 249-255.

Gee, G.E., 1920. Recovering Precious Metals from Waste Liquid Residues: A Complete Workshop Treatise Containing Practical Working Directions for the Recovery of Gold, Silver, and Platinum from Every Description of Waste Liquids in the Jewellery, Photographic, Process Workers, and Electroplating Trade. E. & FN Spon.

Geldenhuis, I.J., Jones, R.T., 2009. Four years of DC arc smelting of PGM-containing oxide feed materials at Mintek. In: *Nickel and Cobalt*, 415–427.

Geng, Q., Zhao, X., Gao, X., Yang, S., Liu, G., 2012. Low-temperature combustion synthesis of CuCr_2O_4 spinel powder for spectrally selective paints. *Journal of Sol-Gel Science and Technology* 61(1), 281–288.

Georgalli, G.A., Eksteen, J.J., Onyango, M.S., Pelsler, M., Lorenzen, L., Aldrich, C., 2008. Fluoride based control of Ca and Mg concentrations in high ionic strength base metal sulfate solutions in hydrometallurgical circuits. *Minerals Engineering* 21(3), 200–212.

Godlewska-żytkiewicz, B., 2004. Preconcentration and separation procedures for the spectrochemical determination of platinum and palladium. *Microchimica Acta* 147(4), 189-210.

Gok, O., 2010. Oxidative Leaching of sulfide ores with the participation of nitrogen species-a review. *Journal of Ore Dressing* 12(24), 22.

Gok, O., Anderson, C.G., 2013. Dissolution of low-grade chalcopyrite concentrate in acidified nitrite electrolyte. *Hydrometallurgy* 134–135, 40–46.

Gok, O., Anderson, C.G., Cicekli, G., Cocen, E.I., 2013. Leaching kinetics of copper from chalcopyrite concentrate in nitrous-sulfuric acid. *Physicochemical Problems of Mineral Processing* 50(1), 399–413.

Gold Fields, 2013. <https://www.goldfields.co.za/gl_exp_arctic.php>.

Gorsuch, R.L., Lehmann, C.S., 2010. Correlation coefficients: Mean bias and confidence interval distortions. *Journal of Methods and Measurement in the Social Sciences* 1(2), 52-65.

Green, B.R., Smit, D.M.C., Maumela, H., Coetzer, G., 2004. Leaching and recovery of platinum group metals from UG-2 concentrates. *Journal of the South African Institute of Mining and Metallurgy* 104(6), 323-331.

Grosse, A.C., Dicoski, G.W., Shaw, M.J., Haddad, P.R., 2003. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy* 69, 1–21.

Grund, S.C., Hanusch, K., Wolf, H.U., 2005. *Arsenic and Arsenic Compounds*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Güntner, J., Hammerschmidt, J., 2012. Sulphating roasting of copper-cobalt concentrates. *Journal of the South African Institute of Mining and Metallurgy* 112(6), 455–460.

Guo, Q., Qu, J.K., Qi, T., Wei, G.Y., Han, B.B., 2012. Activation pretreatment of limonitic laterite ores by alkali-roasting using NaOH. *International Journal of Minerals, Metallurgy, and Materials* 19(2), 100–105.

Guo, X., Li, D., Park, K.H., Tian, Q., Wu, Z., 2009. Leaching behavior of metals from a limonitic nickel laterite using a sulfation–roasting–leaching process. *Hydrometallurgy* 99(3), 144–150.

Habashi, F., 1969. *Principles of Extractive Metallurgy*, vol. 1 CRC Press.

Hamacek, J., Havel, J., 1999. Determination of platinum (II, IV) and palladium (II) as thiocyanate complexes by capillary zone electrophoresis analysis of carboplatin and similar drugs. *Journal of chromatography A* 834, 321–327.

Han, K.N., Kim, P.N.S., 2006. U.S. Patent N° 7,067,090. Washington, DC: U.S. Patent and Trademark Office.

Hancock, R.D., Finkelstein, N.P., Evers, A., 1977. A linear free-energy relation involving the formation constants of palladium (II) and platinum (II). *Journal of Inorganic and Nuclear Chemistry* 39(6), 1031–1034.

Hanf, C.G., 1979. The roasting and leaching of Witwatersrand pyrite concentrates. *Journal of the Southern African Institute of Mining and Metallurgy* 79(13), 365–371.

Hargreaves, J.S., Jackson, S.D., Webb, G. (Eds.), 2006. *Isotopes in heterogeneous catalysis*, vol. 4 World Scientific.

Harjanto, S., Cao, Y., Shibayama, A., Naitoh, I., Nanami, T., Kasahara, K., Okumura, Y., Liu, K., Fujita, T., 2006. Leaching of Pt, Pd and Rh from automotive catalyst residue in various chloride based solutions. *Materials Transactions* 47(1), 129–135.

Harris, G.B., White, C.W., Liu, Z., 2007. Recovery of copper from oxide waste by leaching, ion exchange and electrowinning. Paper presented at Symposium on Copper Hydrometallurgy, Sixth International Copper-Cobre Conference Toronto, August 25–30.

Hawley, E.L., Deeb, R.A., Kavanaugh, M.C., Jacobs, J.A., 2004. Treatment technologies for chromium (VI). *Chromium (VI) handbook*, pp. 275–309.

- Heinen, H.J., Peterson, D.G., Lindstrom, R.E., 1978. Processing Gold Ores Using Heap Leach-Carbon Adsorption Methods. United States Department of the Interior: Bureau of Mines Information Circular 8770.
- Hernandez, J.O., Choren, E.A., 1983. Thermal stability of some platinum complexes. *Thermochimica Acta* 71(3), 265-272.
- Hiroyoshi, N., Miki, H., Hirajima, T., Tsunekawa, M., 2001. Enhancement of chalcopyrite leaching by ferrous ions in acidic ferric sulfate solutions. *Hydrometallurgy* 60, 185–197.
- Holtum, D.A., Murray, D.M., 1994. Bacterial heap leaching of refractory gold/sulphide ores. *Minerals Engineering* 7(5–6), 619–631.
- Horike, C., Morita, K., Okabe, T.H., 2012. Effective dissolution of platinum by using chloride salts in recovery process. *Metallurgical and Materials Transactions B* 43(6), 1300-1307.
- Hourn, M.M., Rohner, P., Bartsch, P., Ngoviky, K., 2005. Benefits of using the Albion Process for a North Queensland Project and a Case Study of Capital and Operating Cost Benefits versus Bacterial Oxidation and Pressure Oxidation.
- Huang, K., Chen, J., Chen, Y.R., Zhao, J.C., Li, Q.W., Yang, Q.X., Zhang, Y., 2006. Enrichment of Platinum Group Metals (PGMs) by two-stage selective pressure leaching cementation from low-grade Pt–Pd sulfide concentrates. *Metallurgical and Materials Transactions B* 37B (October).
- Hunt, A., Kraus, G.A., 2013. Element Recovery and Sustainability (Nº 22). Royal Society of Chemistry.
- Hyvärinen, O., Hämäläinen, M., Lamberg, P., Liipo, J., 2004. Recovering gold from copper concentrate via the HydroCopper™ process. *Journal of The Minerals, Metals & Materials Society* 56(8), 57-59.
- Ishida, K., Kiriya, T., Kuroda, R., 1968. Separation of platinum and palladium from base metals with a weakly basic cellulose ion exchanger. *Analytica Chimica Acta* 41, 537-545.
- Jacob, K.T., Kale, G.M., Waseda, Y., 1992. Gibbs energy of formation of CuCrO_4 and phase relations in the system Cu-Cr-O below 735 K. *Thermochimica Acta* 208, 341–348.
- Jeffrey, M.I., Anderson, C.G., 2003. A fundamental study of the alkaline sulfide leaching of gold. *European Journal of Mineral Processing & Environmental Protection* 3(3).
- Jha, M.K., Lee, J.C., Kim, M.S., Jeong, J., Kim, B.S., Kumar, V., 2013. Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: a review. *Hydrometallurgy* 133, 23–32.

Jones, R.T., 2002. ConRoast: DC arc smelting of dead-roasted sulphide concentrates, *Sulfide Smelting 2002*. Stephens, R.L., Sohn, H.Y. (Eds.), TMS (The Minerals, Metals & Materials Society), Seattle, 17–21 February 2002.

Jones, R.T., 2005. An overview of Southern African PGM smelting. *Nickel and Cobalt 2005: Challenges in Extraction and Production*, 147–178.

Jones, R.T., 2009. Towards commercialisation of Mintek's ConRoast process for platinum smelting. In: *Nickel and Cobalt 2009: Advances in the Processing of Nickel, Cobalt and PGMs using Pyrometallurgical Techniques*, 48th Annual Conference of Metallurgists, 159–168.

Kalichini, M., Corin, K.C., O'Connor, C.T., Simukanga, S., 2017. The role of pulp potential and the sulphidization technique in the recovery of sulphide and oxide copper minerals from a complex ore. *Journal of the Southern African Institute of Mining and Metallurgy* 117(8), 803-810.

Kaminski Jr, E.E., 1970. Anion exchange separations of metal ions in thiocyanate media. PhD Thesis, Iowa State University of Science and Technology, United States of America.

Karimi, A., Golbabaie, F., Mehrnia, M.R., Neghab, M., Mohammad, K., Nikpey, A., Pourmand, M.R., 2013. Oxygen mass transfer in a stirred tank bioreactor using different impeller configurations for environmental purposes. *Iranian Journal of Environmental Health Science and Engineering* 10(1), 1.

Kellogg, H.H., 1964. Critical review of sulfation equilibria. *Transactions of the Metallurgical Society of AIME* 230(7), 1622.

Kerley, B.J., 1983. Recovery of Precious Metals from Difficult Ores. U.S Patent 4,369,061.

Koch, K.R., Burger, M.R., Kramer, J., Westra, A.N., 2006. ¹⁹⁵Pt NMR and DFT computational methods as tools towards the understanding of speciation and hydration/solvation of [PtX₆]²⁻ (X = Cl⁻, Br⁻) anions in solution. *Dalton Transactions* (27), 3277-3284.

Koek, M., Kreuzer, O.P., Maier, W.D., Porwal, A.K., Thompson, M., Guj, P., 2010. A review of the PGM industry, deposit models and exploration practices: implications for Australia's PGM potential. *Resources Policy* 35, 20–35.

Kononova, O.N., Melnikov, A.M., Duba, E.V., 2014. Sorption and Separation of Platinum and Rhodium in Presence of Transition Metals. *Journal of Siberian Federal University. Chemistry* 2(7), 170-184.

Korte, F., Spiteller, M., Coulston, F., 2000. The cyanide leaching gold recovery process is a nonsustainable technology with unacceptable impacts on ecosystems and humans: the disaster in Romania. *Ecotoxicology and Environmental Safety* 46(3), 241–245.

Köse, C.H., 2010. Hydrometallurgical Processing of Lateritic Nickel Ores. MSc Thesis Middle East Technical University, Ankara, Turkey.

Kowalczyk, P., Chmielewski, T., 2008. Search for a New Technology Producing Copper from Chalcopyrite. Scientific Papers of the Institute of Mining, N° 122, Conferences N° 51, 7th PhD Studies Scientific Conference, Interdisciplinary Topics in Mining and Geology, Ofic. Wyd. PWr., Wrocław, 94–100.

Kraemer, D., Junge, M., Bau, M., 2017. Oxidized Ores as Future Resource for Platinum Group Metals: Current State of Research. *Chemie Ingenieur Technik* 89(1-2), 53-63.

Kraemer, D., Junge, M., Oberthür, T., Bau, M., 2015. Improving recoveries of platinum and palladium from oxidized Platinum-Group Element ores of the Great Dyke, Zimbabwe, using the biogenic siderophore Desferrioxamine B. *Hydrometallurgy* 152, 169-177.

Kriek, R.J., 2008. Leaching of Selected PGMs: A Thermodynamic and Electrochemical Study Employing Less Aggressive Lixiviants. MSc Thesis, University of Cape Town, South Africa.

Kshumaneva, E.S., Kasikov, A.G., Gromov, P.B., 2014. Study of the sulfation of platinum containing concentrate of Co-Ni thiospinels. *Russian Journal of Applied Chemistry* 87(2), 128–134.

Kumar, S., Jain, S., 2013. History, introduction, and kinetics of ion exchange materials. *Journal of Chemistry*, 2013.

Kuroda, R., Kiriya, T., Ishida, K., 1968. A specific method for the separation of mercury (II) using a weakly basic cellulose ion exchanger. *Analytica Chimica Acta* 40, 305-310.

Kuzugüdenli, Ö.E., Kantar, Ç., 1999. Alternates to gold recovery by cyanide leaching. *Erciyes Üniversitesi Fen Bilimleri Dergisi* 15(1–2), 119–127.

Kyriakakis, G., 2005. Extraction of gold from platinum group metal (PGM) ores. *Developments in Mineral Processing* 15, 897-917.

La Brooy, S.R., Linge, H.G., Walker, G.S., 1994. Review of gold extraction from ores. *Minerals Engineering* 7(10), 1213–1241.

Landsberg, A., Schaller, J.L., 1971. The kinetics and equilibria of the platinum-chlorine system. *Journal of the Less Common Metals* 23(2), 195-202.

Lawrence, R.W., López, O., 2011. Improving the economics of gold-copper ore projects using SART technology. *Gold 2011*, Montreal, Canada.

Lee, J., Nagaraj, D., Coe, J., 1998. Practical aspects of oxide copper recovery with alkyl hydroxamates. *Minerals Engineering* 11(10), 929-939.

Lee, K., Archibald, D., McLean, J., Reuter, M., 2009. Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Minerals Engineering* 22(4), 395-401.

Lewins, J., 2006. Platinum service. *Mater. World* (January), 30–32.

Lewins, J., Greeaway, T., 2004. The Panton platinum-palladium project. *The Australian Institute of Mining and Metallurgy Bulletin* July-August 04.

Li, J., Miller, J.D., 2006. A review of gold leaching in acid thiourea solutions. *Mineral Processing and Extractive Metallurgy Review* 27, 177–214.

Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012. Thiocyanate hydrometallurgy for the recovery of gold. Part I: chemical and thermodynamic considerations. *Hydrometallurgy* 113–114, 1–9.

Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012. Thiocyanate hydrometallurgy for the recovery of gold. Part II: the leaching kinetics. *Hydrometallurgy* 113–114, 10–18.

Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012. Thiocyanate hydrometallurgy for the recovery of gold Part III: thiocyanate stability. *Hydrometallurgy* 113–114, 19–24.

Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012. Thiocyanate hydrometallurgy for the recovery of gold. Part IV: solvent extraction of gold with Alamine 336. *Hydrometallurgy* 113–114, 25–30.

Li, J., Safarzadeh, M.S., Moats, M.S., Miller, J.D., LeVier, K.M., Dietrich, M., Wan, R.Y., 2012. Thiocyanate hydrometallurgy for the recovery of gold. Part V: process alternatives for solution concentration and purification. *Hydrometallurgy* 113–114, 31–38.

Li, J., Wan, R.Y., LeVier, K.M., Miller, J.D., 2008. Thiocyanate process chemistry for gold recovery. In: Young, C.A., Taylor, P.R., Anderson, C.G., Choi, Y. (Eds.), *Hydrometallurgy 2008, Proceedings of the Sixth International Symposium*. Phoenix, AZ, USA, 824–836.

Li, Y., Kawashima, N., Li, J., Chandra, A.P., Gerson, A.R., 2013. A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. *Advances in Colloid and Interface Science* 197-198, 1-32.

Liddell, K., Newton, T., Adams, M., Muller, B., 2010. Energy consumptions for Kell hydrometallurgical refining versus conventional pyrometallurgical smelting and refining of PGM concentrates. In: *The 4th International Platinum Conference, Platinum in Transition 'Boom or Bust'*, The Southern African Institute of Mining and Metallurgy.

Liddell, K., Newton, T., Adams, M., Muller, B., 2011. Energy consumption for Kell hydrometallurgical refining versus conventional pyrometallurgical smelting and refining of PGM concentrates. *Journal of the South African Institute of Mining and*

Metallurgy 111(2), 127.

Liddell, K.S., Adams, M.D., 2012. Kell hydrometallurgical process for extraction of platinum group metals and base metals from flotation concentrates. *Journal of the Southern African Institute of Mining and Metallurgy* 112(1), 31-36.

Lorenzen, L., Eksteen, J.J., Pelser, M., Aldrich, C., Georgalli, G., 2009. Activated alumina-based adsorption and recovery of excess fluoride ions subsequent to calcium and magnesium removal in base metal leach circuits. *Journal of the South African Institute of Mining and Metallurgy* 109(8), 447–453.

Lorenzen, L., van Deventer, J.S.J., 1992. The mechanism of leaching of gold from refractory ores. *Minerals Engineering* 5(10–12), 1377–1387.

Lottering, M.J., Lorenzen, L., Phala, N.S., Smit, J.T., Schalkwyk, G.A.C., 2008. Mineralogy and uranium leaching response of low grade South African ores. *Minerals Engineering* 21(1), 16-22.

Lu, Z.Y., Jeffrey, M.I., Lawson, F., 2000. The effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy* 56, 189–202.

Lundström, M., 2009. Chalcopyrite Dissolution in Cupric Chloride Solutions. PhD Thesis, Helsinki University of Technology, Finland.

Lundström, M., Aromaa, J., Forsen, O., 2009. Redox potential characteristics of cupric chloride solutions. *Hydrometallurgy* 95, 285–289.

Lundström, M., Aromaa, J., Forsen, O., Hyvarinen, O., Barker, M.H., 2005. Leaching of chalcopyrite in cupric chloride solution. *Hydrometallurgy* 77, 89–95.

Lundström, M., Aromaa, J., Forsen, O., Hyvarinen, O., Barker, M.H., 2007. Cathodic reactions of Cu^{2+} in cupric chloride solution. *Hydrometallurgy* 85, 9–16.

Luszczkiewicz, A., Chmielewski, T., 2008. Acid treatment of copper sulfide middlings and rougher concentrates in the flotation circuit of carbonate ores. *International Journal of Mineral Processing* 88(1), 45-52.

Mahmoud, M.H., 2003. Leaching platinum-group metals in a sulfuric acid/chloride solution. *Journal of the Minerals, Metals and Materials Society* 55(4), 37-40.

Malik, P., Paiva, A.P., 2010. A novel solvent extraction route for the mutual separation of platinum, palladium, and rhodium in hydrochloric acid media. *Solvent Extraction and Ion Exchange* 28(1), 49-72.

Marsden, J.O., Brewer, R.E., Hazen, N., 2003. Copper concentrate leaching developments by Phelps dodge corporation. In: Young, C.A., Alftmtazi, A.M., Anderson, C.G., Dreisinger, D.B., Harris, B., James, A. (Eds.), *Hydrometallurgy 2003 – Fifth International Conference in Honour of Professor Ian Ritchie: Electrometallurgy and Environmental Hydrometallurgy*, vol. 2, TMS (The Minerals, Metals & Materials Society).

Mateos, F.B., Perez, I.P., Mora, F.C., 1987. The passivation of chalcopyrite subjected to ferric sulfate leaching and its reactivation with metal sulfides. *Hydrometallurgy* 19, 159–167.

Maurice, D., Hawk, J.A., 1999. Ferric chloride leaching of a mechanically activated pentlandite–chalcopyrite concentrate. *Hydrometallurgy* 52, 289–312.

Mayze, R., 1999. An engineering comparison of the three treatment flowsheets in WA nickel laterite projects. In: *Proceedings ALTA Nickel/Cobalt Pressure Leaching & Hydrometallurgy Forum*.

McInnes, C.M., Sparrow, G.J., Woodcock, J.T., 1994. Extraction of platinum, palladium and gold by cyanidation of Coronation Hill ore. *Hydrometallurgy* 35, 141–159.

McKevitt, B.R., 2007. Removal of iron by ion exchange from copper electrowinning electrolyte solutions containing antimony and bismuth. Doctoral dissertation, University of British Columbia, Canada.

Meersbergen, M.T., Lorenzen, L., Deventer, J.S.J., 1993. The electrochemical dissolution of gold in bromine medium. *Minerals Engineering* 6(8–10), 1067–1079.

Mertie, J.B., 1969. *Economic geology of the platinum metals*. US Government Printing Office.

Miezitis, Y., 2014. *Australia's Identified Mineral Resources 2013*. Commonwealth of Australia (Geoscience Australia) 2014. ISSN: 1327-1466.

Mihaylov, I., 2003. Solvent extractants for nickel and cobalt: new opportunities in aqueous processing. *Journal of the Minerals, Metals, and Materials Society* 55(7), 38–42.

Milbourne, J., Tomlinson, M., Gormely, L., 2003. Use of hydrometallurgy in direct processing of base metal/PGM concentrates. *Hydrometallurgy*, 625.

Mohammed, N., Ahmad, W.A., 2010. Application of Response Surface Methodology (RSM) for optimizing removal of Cr(VI) wastewater using Cr(VI)-reducing biofilm systems. In: *Proceedings of Regional Annual Fundamental Science Seminar 2010*.

Mountain, B.W., Wood, S.A., 1988. Chemical controls on the solubility, transport, and decomposition of platinum and palladium in hydrothermal solutions: a thermodynamic approach. *Economic Geology* 83, 492–510.

Moyes, J., Crescent, M., 1999. *The INTEC copper process*. Copper.

Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2014. Evaluation of the Merrill-Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solutions. *Hydrometallurgy* 142, 36–46.

- Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2014. The extraction of Pt, Pd and Au from an alkaline cyanide simulated heap leachate by granular activated carbon. *Minerals Engineering* 55, 11–17.
- Mpinga, C.N., Eksteen J.J., Aldrich, C., Dyer, L., 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review. *Minerals Engineering* 78, 93-113.
- Mpinga, C.N., Eksteen J.J., Aldrich, C., Dyer, L., 2017. Identification of the significant factors determining extractability of Ni and Cu after sulfation roasting of a PGM-bearing chromitite ore. *Minerals Engineering* 110, 153-165.
- Mpinga, C.N., Eksteen, J.J., Aldrich C., Dyer, L., 2018. Atmospheric leach process of high-chromitite PGM-bearing oxidized mineralized ore through a single-stage and two-stage techniques. *Minerals Engineering* 125, 165-175.
- Mpinga, C.N., Eksteen, J.J., Aldrich C., Dyer, L., 2018. A conceptual hybrid process flowsheet for platinum group metals (PGMs) recovery from a chromite-rich Cu-Ni PGM bearing ore in oxidized mineralization through a single-stage leach and adsorption onto ion exchange resin. *Hydrometallurgy* 178, 88-96.
- Muir, D.M., 2011. A review of the selective leaching of gold from oxidised copper–gold ores with ammonia–cyanide and new insights for plant control and operation. *Minerals Engineering* 24, 576–582.
- Muir, D.M., Ariti, J., 1991. Studies on the dissolution of platinum and palladium from low grade ores and by-products. In 5th AusIMM Extractive Metallurgy Conference, Perth, Australia (2-4 Oct., 1991), 183-186.
- Munoz, G.A., Miller, J.D., 1999. Noncyanide Leaching of an Auriferous Pyrite Ore from Ecuador. For Presentation at the Society for Mining, Metallurgy, and Exploration, Inc., Annual Meeting Denver, Colorado, March 1–3, 1999.
- Mwase, J., 2009. Hydrometallurgical Extraction of Platinum Group Metals from a Low-Grade Ore Concentrate. MSc Thesis, University of Cape Town, South Africa.
- Mwase, J.M., Petersen, J., 2017. Characterizing the leaching of sperrylite (PtAs₂) in cyanide based solutions. *Hydrometallurgy* 172, 1-10.
- Mwase, J.M., Petersen, J., Eksteen, J.J., 2012. A conceptual flowsheet for heap leaching of platinum group metals (PGMs) from a low-grade ore concentrate. *Hydrometallurgy* 111-112, 129-135.
- Mwase, J.M., Petersen, J., Eksteen, J.J., 2012. Assessing a two-stage heap leaching process for Platreef flotation concentrate. *Hydrometallurgy* 129-130, 74-81.
- Mwase, J.M., Petersen, J., Eksteen, J.J., 2014. A novel sequential heap leach process for treating crushed Platreef ore. *Hydrometallurgy* 141, 97-104.
- Navisa, J., Sravya, T., Swetha, M., Venkatesan, M., 2014. Effect of bubble size on aeration process. *Asian Journal of Scientific Research* 7(4), 482.

Nayar, M.R., Watson, H.E., Sudborough, J.J., 2013. Reactions of chromates at high temperatures. Part 1. The synthesis and decomposition of calcium, sodium and magnesium chromates in air. *Journal of the Indian Institute of Science* 7(IV), 53–70.

Nazari, G., Asselin, E., 2009. Morphology of chalcopyrite leaching in acidic ferric sulfate media. *Hydrometallurgy* 96, 183–188.

Nazari, G., Dixon, D.G., Dreisinger, D.B., 2011. Enhancing the kinetics of chalcopyrite leaching in the Galvanox™ process. *Hydrometallurgy* 105, 251–258.

Nazari, G., Dixon, D.G., Dreisinger, D.B., 2012. The mechanism of chalcopyrite leaching in the presence of silver-enhanced pyrite in the Galvanox™ process. *Hydrometallurgy* 113–114, 122–130.

Nazari, G., Dixon, D.G., Dreisinger, D.B., 2012. The role of galena associated with silver-enhanced pyrite in the kinetics of chalcopyrite leaching during the Galvanox™ process. *Hydrometallurgy* 113–114, 177–184.

Nazari, G., Dixon, D.G., Dreisinger, D.B., 2012. The role of silver-enhanced pyrite in enhancing the electrical conductivity of sulfur product layer during chalcopyrite leaching in the Galvanox™ process. *Hydrometallurgy* 111–112, 35–45.

Nazari, G.T., 2012. Enhancing the Kinetics of Pyrite Catalyzed Leaching of Chalcopyrite. PhD Thesis, University of British Columbia, Canada.

NEPC, 2004. Review of the Practicability of a 10 min Sulfur Dioxide Standard. National Environment Protection (Ambient Air Quality) Measure, Issues Paper March 2004.

Newell, A., Bradshaw, D., Harris, P., 2006. The effect of heavy oxidation upon flotation and potential remedies for Merensky type sulfides. *Minerals Engineering* 19(6), 675-686.

Nikoloski, A.N., Ang, K.L., 2014. Review of the application of ion exchange resins for the recovery of platinum-group metals from hydrochloric acid solutions. *Mineral Processing and Extractive Metallurgy Review* 35(6), 369-389.

Nikoloski, A.N., Ang, K.L., Li, D., 2015. Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins. *Hydrometallurgy* 152, 20-32.

Norrgran, D.A., 1985. U.S. Patent N° 4,541,993. U.S. Patent and Trademark Office, Washington DC, United States of America.

Oberthür, T., Melcher, F., Buchholz, P., Locmelis, M., 2013. The oxidized ores of the main sulphide zone, Great Dyke, Zimbabwe: turning resources into minable reserves-mineralogy is the key. *Journal of the Southern African Institute of Mining and Metallurgy* 113(3), 191-201.

Okamoto, H., 1990. The As-Pt (Arsenic-Platinum) system. *Journal of Phase Equilibria* 11(5), 508-510.

- Oleschuk, R.D., Chow, A., 1998. The separation of platinum and palladium by selective extraction of $\text{H}_2\text{Pt}(\text{SCN})_6$ and $\text{H}_2\text{Pd}(\text{SCN})_4$ using a polyTHF impregnated filter. *Talanta* 45(6), 1235–1245.
- Olivotos, S., Economou-Eliopoulos, M., 2016. Gibbs Free Energy of Formation for Selected Platinum Group Minerals (PGM). *Geosciences* 6(1), 2.
- Oraby, E., Eksteen, J.J., 2013. A Process of Precious Metals Recovery. Australian Provisional Patent Application N° 2,013,903,380.
- Oraby, E.A., Eksteen, J.J., 2014. The selective leaching of copper from a gold–copper concentrate in glycine solutions. *Hydrometallurgy* 50, 14–19.
- Palmer, C.M., Johnson, G.D., 2005. The Activox® Process: Growing significance in the nickel industry. *Journal of The Minerals, Metals & Materials Society* 57(7), 40–47.
- Parirenyatwa, S., Escudero-Castejon, L., Sanchez-Segado, S., Hara, Y., Jha, A., 2016. Comparative study of alkali roasting and leaching of chromite ores and titaniferous minerals. *Hydrometallurgy* 165, 213–226.
- Pasandideh, S.H.R., Niaki, S.T.A., 2006. Optimizing multi-response statistical problems using a genetic algorithm. *Scientia Iranica* 13(1), 50–59.
- Passos, C.G., Ribaski, F.S., Simon, N.M., dos Santos, A.A., Vaghetti, J.C., Benvenuti, E.V., Lima, É.C., 2006. Use of statistical design of experiments to evaluate the sorption capacity of 7-amine-4-azaheptylsilica and 10-amine-4-azadecylsilica for Cu(II), Pb(II), and Fe(III) adsorption. *Journal of Colloid and Interface Science* 302(2), 396–407.
- Paunovic, M., Schlesinger, M., 2006. Fundamentals of electrochemical deposition (Vol. 45). John Wiley & Sons.
- Pesavento, M., Sturini, M., D'Agostino, G., Biesuz, R., 2010. Solid phase extraction of copper (II) by fixed bed procedure on cation exchange complexing resins. *Journal of Chromatography A* 1217(8), 1208–1218.
- Phillips, R.E., Jones, R.T., Chennells, P., 2008. Commercialization of the ConRoast process. In: Third International Platinum Conference 'Platinum in Transformation', The Southern African Institute of Mining and Metallurgy.
- Prasad, M.S., Mensah-Biney, R., Pizarro, R.S., 1991. Modern trends in gold processing— overview. *Minerals Engineering* 4(12), 1257–1277.
- Prasad, S., Pandey, B.D., 1998. Alternative processes for treatment of chalcopyrite — A review. *Minerals Engineering* 11(8), 763–781.
- Prasad, S., Pandey, B.D., 1999. Sulphation roasting studies on synthetic copper–iron sulphides with steam and oxygen. *Canadian metallurgical quarterly* 38(4), 237–247.

Pugaev, D., Nicol, M., Senanayake, G., 2011. The mechanisms of the passivation of sulfide minerals in oxidative leaching processes. In: 6th Southern African Base Metals Conference, The Southern African Institute of Mining and Metallurgy, 2011.

Qi, T.G., Liu, N., Li, X.B., Peng, Z.H., Liu, G.H., Zhou, Q.S., 2011. Thermodynamics of chromite ore oxidative roasting process. *Journal of Central South University of Technology* 18(1), 83-88.

Rambiyana, R., Den Hoed, P., Garbers-Craig, A.M., 2014. Fire and brimstone: The roasting of a PGM concentrate. In: The 6th International Platinum Conference, 'Platinum-Metal for the Future'. The Southern African Institute of Mining and Metallurgy, pp. 2014.

Renner, H., Schlamp, G., Kleinwächter, I., Drost, E., Lüscho, H.M., Tews, P., Panster, P., Diehl, M., Lang, J., Kreuzer, T., Knödler, A., 2001. Platinum group metals and compounds. *Ullmann's Encyclopedia of Industrial Chemistry*.

Rhoades, R.A., Bell, D.R., 2012. *Medical Physiology: Principles for Clinical Medicine*. Lippincott Williams & Wilkins.

Ritchie, S., Eksteen, J.J., 2011. Investigating the effect of slag bath conditions on the existence of "mushy" zones in PGM smelting furnaces using computational fluid dynamics. *Minerals Engineering* 24(7), 661–675.

Robins, R.G., Jayaweera, L.D., 1992. Arsenic in gold processing. *Mineral Processing and Extractive Metallurgy Review* 9(1-4), 255-271.

Rosia Montana Gold Corporation S.A., 2007. *Flowsheet and Leaching Alternatives for the Rosia Montana Flowsheet*. Processing and Leaching Alternatives.

Rumiantsev, D.V., Popov, V.A., Tsemekhman, L.S., 2016. Development of a roasting process for arsenic gold-bearing concentrates to recover arsenic into a low-toxic product and produce calcine suitable for further processing. *Journal of Siberian Federal University Engineering and Technology* 9(6), 811.

Saari, T., 2005. *Platinum Exploration and Mining in Finland – An Overview*. Invest in Finland, Aleksanterinkatu 17 P.O. Box 800, FIN-00101 Helsinki, Finland.

Safarzadeh, M.S., Miller, J.D., Huang, H.H., 2014. Thermodynamic analysis of the Cu-As-S-(O) system relevant to sulfuric acid baking of enargite at 473 K (200°C). *Metallurgical and Materials Transactions B* 45(2), 568–581.

Sammut, D., Welham, N.J., 2002. The Intec copper process: a detailed environmental analysis. In: *Green Processing Conference*, 29–31 May 2002.

Sanders, J.F., 1926. *Process of Extracting Arsenide from Ores*. United States Patent 1,581,475.

Sceresini, B., 2005. Gold-copper ores. *Developments in Mineral Processing* 15, 789–824.

Schlecht, L., 1958. U.S. Patent N° 2,829,967. Washington, DC: U.S. Patent and Trademark Office.

Schoeman, E., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., 2012. The Recovery of Platinum, Palladium, and Gold from a Cyanide Heap Solution, with Use of Ion Exchange Resins. The Southern African Institute of Mining and Metallurgy Platinum.

Sefako, R., Sekgarametso, K., Sibanda, V., 2017. Potential Processing Routes for Recovery of Platinum Group Metals from Southern African Oxidized PGM Ores: A Review. *Journal of Sustainable Metallurgy* 3(4), 797-807.

Senanayake, G., 2004. Fundamentals and applications of metal–ligand complexes of gold(I/III) in non-cyanide gold processes. In: Green Processing Conference Fremantle, Western Australia, 10–12 May 2004.

Senanayake, G., 2004. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications. *Minerals Engineering* 17, 785–801.

Senanayake, G., 2009. A review of chloride assisted copper sulfide leaching by oxygenated sulfuric acid and mechanistic considerations. *Hydrometallurgy* 98, 21–32.

SenthilKumar, P., Ramalingam, S., Abhinaya, R.V., Kirupha, S.D., Vidhyadevi, T., Sivanesan, S., 2012. Adsorption equilibrium, thermodynamics, kinetics, mechanism and process design of zinc (II) ions onto cashew nut shell. *The Canadian Journal of Chemical Engineering* 90(4), 973-982.

Shaik, K., Petersen, J., 2017. An investigation of the leaching of Pt and Pd from cooperite, sperrylite and column bioleached concentrates in thiocyanate-cyanide systems. *Hydrometallurgy* 173, 210-217.

Shams, K., Goodarzi, F., 2006. Improved and selective platinum recovery from spent α -alumina supported catalysts using pretreated anionic ion exchange resin. *Journal of hazardous materials* 131(1), 229-237.

Sheridan, M.S., Nagaraj, D.R., Fornasiero, D., Ralston, J., 2002. The use of a factorial experimental design to study collector properties of N-allyl-O-alkyl thionocarbamate collector in the flotation of a copper ore. *Minerals Engineering* 15(5), 333–340.

Shin, Y.J., Chang, J.W., Kim, J.H., Park, B.H., Lee, K.Y., Lee, W.J., Chang, J.H., 2009. A dynamic simulation of the sulfuric acid decomposition process in a sulfur-iodine nuclear hydrogen production plant. *Nuclear Engineering and Technology* 41(6), 831–840.

Sibrell, P.L., Atkinson, G.B., Walters, L.A., 1994. Cyanide Leaching Chemistry of Platinum-Group Metals. US Department of Interior, Bureau of Mines.

Singh, K.K., Shenoy, K.T., Rao, H., Ghosh, S.K., 2011. Flow simulations of industrial scale agitated tanks. *BARC Newsletter* 8–15.

Smith, B., Moody, P., 1991. The Use of DEAE-cellulose to extract anionic organic material from groundwaters. EUR Luxembourg.

Snyders, C.A., Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., 2012. The Adsorption and Elution of Platinum Group Metals (Pt, Pd, and Au) from Cyanide Leach Solutions using Activated Carbon. The Southern African Institute of Mining and Metallurgy Platinum.

Snyders, C.A., Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Eksteen, J.J., 2013. The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions. Journal of the Southern African Institute of Mining and Metallurgy 113.

Sohn, H.Y., Wadsworth, M.E., 2013. Rate Processes of Extractive Metallurgy. Springer Science & Business Media.

Sole, K.C., Feather, A.M., Cole, P.M., 2005. Solvent extraction in southern Africa: An update of some recent hydrometallurgical developments. Hydrometallurgy 78(1), 52-78.

Sparrow, G.J., Woodcock, J.T., 1995. Cyanide and other lixiviant leaching systems for gold with some practical applications. Mineral Processing and Extractive Metallurgy Review 14(3-4), 193-247.

Stange, W., 1999. The process design of gold leaching and carbon-in-pulp circuits. Journal of the Southern African Institute of Mining and Metallurgy 99(1), 13–25.

Staunton, W.P., 2005. Carbon-in-pulp. Developments in Mineral Processing 15, 562–587.

Stauter, J.C., Um, R.T., 1977. U.S. Patent N° 4,029,734. U.S. Patent and Trademark Office, Washington DC, United States of America.

Tatarnikov, A.V., Sokolskaya, I., Shneerson, Y.M., Lapin, A.Y., Goncharov, P.M., 2004. Treatment of platinum flotation products. Platinum Metals Review 48(3), 125-132.

Tathavakar, V.D., Antony, M.P., Jha, A., 2005. The physical chemistry of thermal decomposition of South African chromite minerals. Metallurgical and Materials Transactions B 36(1), 75–84.

Teng, T.T., Low, L.W., Yusup, Y., 2012. Heavy Metal Ion Extraction Using Organic Solvents: An Application of the Equilibrium Slope Method. INTECH Open Access Publisher.

Tinoco, R., Acevedo, A., Galindo, E., Serrano-Carreón, L., 2011. Increasing *Pleurotus ostreatus* laccase production by culture medium optimization and copper/lignin synergistic induction. Journal of Industrial Microbiology and Biotechnology 38(4), 531–540.

- Trexler, D.T., Flynn, T., Hendrix, J.L., 1990. Heap leaching. *Geo-Heat Center Bull.* (Summer).
- Trickey, S., 2010. Options for PGM supply outside of Africa. In: *The 4th International Platinum Conference, Platinum in Transition 'Boom or Bust'*, The Southern African Institute of Mining and Metallurgy.
- Tshiongo, N., Mbaya, R.K.K., Maweja, K., Tshabalala, L.C., 2010. Effect of cooling rate on base metals recovery from copper matte smelting slags. *World Academy of Science, Engineering and Technology* 4, 236–240.
- Turkmen, Y., Kaya, E., 2009. Acidified ferric chloride leaching of a chalcopyrite concentrate. *Journal of Ore Dressing* 11(22).
- Turner, D.W., Hourn, M., 2013. *Albion Process Simplicity in Leaching: Copper Applications*. Xstrata Technology.
- Udupa, M.R., 1982. Thermal decomposition of cerium (IV), cerium (III), chromium (III) and titanium (IV) sulphates. *Thermochimica Acta* 57(3), 377–381.
- Ustaoğlu, E., Geveci, A., 2007. Hot filtration: a way to enhance the recovery of chromite in sulfuric acid leaching, with or without the addition of perchloric acid. *Turkish Journal of Engineering and Environmental Science* 30(6), 375–380.
- Valenzuela, A., 2000. *Arsenic Management in the Metallurgical Industry*. PhD Thesis Université Laval, Quebec City, Quebec, Canada.
- Venkatesh, V., Pilchak, A.L., Allison, J.E., Ankem, S., Boyer, R.R., Christodoulou, J., Fraser, H.L., Imam, M.A., Kosaka, Y., Rack, H.J., Chatterjee, A., Woodfield, A., 2016. *Proceedings of the 13th World Conference on Titanium*. John Wiley & Sons.
- Vermaak, C.F., 1995. *The Platinum-Group Metals: A Global Perspective*. Mintek, Randburg, South Africa.
- Vukcevic, S., 1996. A comparison of alkali and acid methods for the extraction of gold from low grade ores. *Minerals Engineering* 9(10), 1033–1047.
- Waitz Jr, H.W., 1982. Ion exchange for recovery of precious metals. *Plating and Surface Finishing* 69(4), 56-59.
- Walker, S.R., Jamieson, H.E., Lanzirrotti, A., Hall, G.E.M., Peterson, R.C., 2015. The effect of ore roasting on arsenic oxidation state and solid phase speciation in gold mine tailings. *Geochemistry: Exploration, Environment, Analysis* 15(4), 273–291.
- Wan, R.Y., LeVier, K.M., 2011. Precious Metal Recovery using Thiocyanate Lixiviant. US Patent 7,947,108 B2.
- Wan, R.Y., LeVier, M., Miller, J.D., 1993. Research and development activities for the recovery of gold from noncyanide solutions. In: Hisky, J.B., Warren, G.W. (Eds.), *Hydrometallurgy Fundamentals, Technology and Innovation*, pp. 415–436.

Wang, S., 2005. Copper leaching from chalcopyrite concentrates. *Journal of The Minerals, Metals & Materials Society* 57(7), 48-51.

Warshawsky, A., 1983. Ion Exchange Separation of Platinum and Palladium by Nucleophilic Displacement With Thiocyanate or Thiourea^{1,2}. *Separation and Purification Methods* 12(1), 37-48.

Weber, D., 1997. Method Development in Solid Phase Extraction using ISOLUTE® SAX and ISOLUTE PE-AX SPE Columns for the Extraction of Aqueous Samples. Technical note 103.

Wilburn, D.R., 2012. Global Exploration and Production Capacity for Platinum-Group Metals from 1995 through 2015.

Wilburn, D.R., Bleiwas, D.I., 2004. Platinum-Group Metals-World Supply and Demand. U.S. Geological Survey Open-File Report 2004-1224.

Wilkomirsky, I., 2014. Dynamic simulation of processing high-arsenic copper concentrates in a fluidized bed roaster. Presented at SME Annual Meeting/Exhibit, February 24-26, 2014, Salt Lake City, UT, USA.

Winand, R., 1991. Chloride hydrometallurgy. *Hydrometallurgy* 27, 285–316.

WPIC., 2014. The World Platinum Investment Council. Press Release. London, 03 December 2014.

Xiao, Z., Laplante, A.R., 2004. Characterizing and recovering the platinum group Minerals – a review. *Minerals Engineering* 17, 961–979.

Yang, X., Shi, X., Xu, H., Moats, M.S., Miller, J.D., Xiao, X., Ma, L., 2011. Leaching of gold in acid thiourea-thiocyanate solutions using ferric sulfate as oxidant. In: TMS 2011 140th Annual Meeting and Exhibition, Materials Processing and Energy Materials, vol. 1. John Wiley & Sons, p. 299.

Yeates, R.C., Somorjai, G.A., 1983. The growth and alloy formation of copper on the platinum (111) and stepped (553) crystal surfaces; characterization by LEED, AES, and CO thermal desorption. *Surface Science* 134(3), 729-744.

Yu, D., Utigard, T.A., Barati, M., 2012. Leaching behavior of the roasted nickel calcine. Proceedings of the 51st Annual Conference of Metallurgists of CIM (COM 2012), Canada.

Yu, D., Utigard, T.A., Barati, M., 2014. Fluidized bed selective oxidation-sulfation roasting of nickel sulfide concentrate: Part I. Oxidation roasting. *Metallurgical and Materials Transactions B* 45(2), 653–661.

Yu, D., Utigard, T.A., Barati, M., 2014. Fluidized bed selective oxidation-sulfation roasting of nickel sulfide concentrate: Part II. Sulfation roasting. *Metallurgical and Materials Transactions B* 45(2), 662–674.

Zanjani, A., Baghalha, M., 2009. Factors affecting platinum extraction from used reforming catalysts in iodine solutions at temperatures up to 95°C. *Hydrometallurgy* 97, 119–125.

Zhang, Y., Liu, S., Xie, H., Zeng, X., Li, J., 2012. Current status on leaching precious metals from waste printed circuit boards. *Procedia Environmental Science* 16, 560–568.

Zhao, Y., Hou, Y., Cui, Y., Liang, H., Li, L., 2015. Recovery of copper from copper sulfide concentrate by sulfation roasting. *International Journal of Nonferrous Metallurgy* 4(02), 9–13.

Zhou, L., Liu, J., Liu, Z., 2009. Adsorption of platinum(IV) and palladium(II) from aqueous solution by thiourea-modified chitosan microspheres. *Journal of Hazardous Materials* 172, 439-446.

Zhou, S., Wei, Y., Li, B., Wang, H., Ma, B., Wang, C., 2016. Mechanism of sodium chloride in promoting reduction of high-magnesium low-nickel oxide ore. *Scientific Reports*, 6.

Zipperian, D.C., Raghavan, S., 1985. The recovery of vanadium from dilute acid sulfate solutions by resin ion exchange. *Hydrometallurgy* 13(3), 265-281.

Zolgharnein, J., Shahmoradi, A., 2010. Adsorption of Cr(VI) onto *Elaeagnus* tree leaves: statistical optimization, equilibrium modeling, and kinetic studies. *Journal of Chemical & Engineering Data* 55(9), 3428-3437.

"Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged."