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EXTRACTION OF PLATINUM, PALLADIUM AND RHODIUM
FROM TAILINGS BY A METAL CHLORIDE BASED LEACH
REAGENT.

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A Dissertation submitted to the Faculty of
Engineering, University of the Witwatersrand,
Johannesburg, in fulfillment of the requirements for
the Degree of Master of Science in Engineering.

Johannesburg, 1993

Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

Archie

10 day of February, 1993

Abstract

High extractions of the platinum group metals from a refractory tailings concentrate (PGM Concentration : Pt 81.5ppm, Pd 21.5ppm, Rh 17.5ppm) was achieved after short low-temperature roasting and subsequent leaching with a zinc chloride based leach reagent containing nitric acid under atmospheric pressure at temperatures from 105°C to 120°C.

A one stage, 2.5 to 3 hour leach resulted in the following extractions :

Platinum 90.85% ; Palladium 79.46% ; Rhodium 80.12%

The zinc chloride based leach reagent allowed for the use of a higher leaching temperature than which is found in Aqua Regia. This higher leaching temperature resulted in the levels of extractions of platinum, palladium and rhodium being comparable with one another.

Extractions were not effected within a zinc chloride concentration range of 2M to 6M.

Also an oxidant concentration range of 5.48% to 24.97% resulted in similar degrees of extraction.

It was established that the main limiting factor for the dissolution of the platinum group metals was the accessibility of the leach reagent towards platinum, palladium and rhodium. This was over come by roasting.

Acknowledgements

I acknowledge with gratitude the help of the following people, whose support and assistance made the completion of this dissertation possible.

Dr. F.K. Letowski, my supervisor, who provided guidance and advice throughout; Dr. D.R. Arnold and Dr. H.A.H. Laue for their support and encouragement.

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Aim Of Research

To establish if a metal chloride based leach reagent could be used for the extraction of the platinum group metals from a refractory tailings concentrate.

Specifically to establish the effect of the following parameters,

1. Pre-Leach Treatment of Concentrate - Roasting
2. Metal Chloride Concentration
3. Oxidant Concentration
4. Leaching Temperature
5. Leaching Time

on the degree of extraction of platinum, palladium and rhodium.

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Introduction

The Platinum Group Metals comprise of Platinum (Pt), Palladium (Pd), Iridium (Ir), Osmium (Os), Ruthenium (Ru) and Rhodium (Rh). All are analogous with silver and gold and are invariably present as native alloys of the platinum metal.

The Indians of Ecuador and Columbia were the first to collect platinum nuggets to produce primitive articles as well as a crude platinum-gold alloy, in which platinum nuggets were hammered flat and soldered together with molten gold. The Spanish named platinum, platina, which means little silver and regarded it as an impurity.⁽¹⁾

Platinum was first discovered in Columbia and mining began in 1778. Rich platinum placers were found in the Russian Ural mountains in 1822. Platinum was found in the Bushveld complex in Transvaal, South Africa in the latter part of 1924 on the farm Maandagshoek and named after its discoverer the Merensky Reef.⁽²⁾

South Africa, Russia and Canada account for nearly all of the worlds mined primarily platinum group metals. South Africa and Bophuthatswana possess approximately 70% of the world's reserves of platinum group metals and currently provide an estimated 83% of the western world's annual production.

South African deposits are termed the Bushveld Igneous Complex, a stratiform intrusion that covers an estimated area of 650 000 square kilometers in the central Transvaal.

It is believed to be the world's largest known repository of platinum group metals containing an estimated reserve of more than 200 million oz of platinum group metals.

Platinum Group Metal Recovery

The conventional methods used for the recovery of platinum group metals involves primarily pyrometallurgical processing techniques. The flotation or gravity concentrate is prepared from the crushed ore. This concentrate is then fed into a smelter, from which a matte of base metals is obtained. The platinum group metals are then recovered from the base metals matte by known techniques, for example pressure leaching, electro refining, (3) (4)

The advantage of this pyrometallurgical process is that, at smelting temperatures, the ore minerals lose their identity in a molten mass. Accordingly, thermodynamics, mass transfer kinetics and phase separations are the main factors which control the process.

In the smelting process, sulfur (from the sulphidic ores) supplies part of the fuel energy.

However, SO_2 leakage into the atmosphere is prohibited resulting in a conflicting situation between energy consumption and environmental problems.

But, the biggest problem of this conventional smelting process lies within obtaining a suitable concentrate. The grade of the concentrate as well as its composition has to conform to certain specifications in order for it to be suitable for smelting.

For example: If the chromite content of the concentrate is too high, it can result in the formation of infusible slag which contains a high proportion of unrecoverable platinum group metals. That is, the tendency of the chromite to "freeze" within the slag and build up in the furnace.

Thus as a result of this tendency, it is often necessary to sacrifice some recovery during the flotation or gravity concentration process in order to achieve the grade of concentrate that will be suitable for smelting.

This sacrificing of recovery during the concentration process results in loss of platinum group metals.

As an alternative to the conventional pyrometallurgical process, a hydrometallurgical process after preparation of the flotation or gravity concentrate is proposed.

In such a process the valuable constituents in the concentrate, such as the platinum group metals as well as base metals, could be extracted by a suitable leaching reagent. Resulting in the formation of a solution of these metals. This enriched solution can then be separated from the remaining gangue material, particularly the insoluble chromite, by simple filtration. The platinum group metals and desired base metals could then be recovered from the leach solution by using conventionally known hydrometallurgical techniques.

One of the main reasons why such a chloride hydrometallurgical process has not been exploited to any large degree, is due primarily to the fact that it is extremely difficult to find a suitable leaching reagent that will dissolve the platinum group metals in the concentrate. The platinum group metals are present in the concentrate as a number of mineral compounds, some of which are insoluble, others are encapsulated within other minerals such as pentlandite or chalcopyrite.

A review of chloride-based systems in hydrometallurgy indicates that it has been used for the treatment and recovery of precious metals for a number of years.⁽⁵⁾ The earliest use of chloride ions in metallurgy seem to appear during the sixteenth century for the amalgamation of silver. The next important process was the direct decomposition of silver sulphide by cuprous chloride, developed in 1860.⁽⁶⁾ This can be considered as the start of direct hydrometallurgy of sulphides.

The usage of chloride chemistry in hydrometallurgy has suffered in its application due mainly to the highly corrosive character of the chloride ion, which can penetrate normally passive layers on a high-alloy nickel-chromium steel.⁽⁷⁾ However, with the advent of new materials this problem can be solved and the possibility of applying chloride chemistry presents itself in new ways.

The attractive features of chloride-based hydrometallurgy can be summarized as follows⁽⁴⁾⁽⁸⁾:

- (i) Many metal chloride salts have a high solubility, thus allowing for the use of highly concentrated metal solutions.

- (ii) The formation of metal chlorocomplex ions in solution enables a number of important metal separations to be achieved more readily in chloride solutions.
- (iii) Hydrochloric acid is often more readily recoverable from chloride solutions; thus allowing regeneration and recycling of the chloride within the process.
- (iv) High concentrated solutions of most metals of interest in non-ferrous metallurgy can be obtained through complexation by chloride ions.
- (v) Most electrochemical reactions are more readily reversible in chloride solutions.
- (vi) Leaching of sulphide occurs more easily in chloride solutions.

Disadvantages

- (i) Chloride solutions are corrosive. However, this can be matched by choosing suitable materials for equipment.
- (ii) Solid residues should be thoroughly washed before being disposed as wastes or environmental protection.

Choice Of Leaching Solution

The leaching solution needs to be based on chloride compounds which will be non-volatile under the leach conditions.

The decomposition of platinum group metals, their refractory compounds and the formation of soluble chloride complexes in solution depend on three important parameters.

1. Temperature.

The kinetics of platinum group metal dissolution, their liberation from refractory minerals and the kinetics of platinum group metal sulphide and arsenide oxidation are highly dependent on temperature.

2. Chloride Concentration.

Any reaction in which the soluble complex chlorides are formed with dissolved metals will be driven towards completion by the presence of a high chloride concentration in the leach solution.

3. Type and Effectiveness of Oxidant.

Dissolution of platinum group metals requires a high chloride ion concentration in an acidic solution, together with the presence of a suitable oxidant. Such conditions exist when Aqua Regia is used as a leaching reagent. Aqua Regia is a mixture of concentrated hydrochloric and nitric acids in the proportion of $[HCl]:[HNO_3]$ 3:1.

However, even at a relatively low temperature ($70^{\circ}C-90^{\circ}C$), leaching with Aqua Regia is extremely difficult due to the instability of the solution, which is marked by a high partial pressure of gaseous hydrogen chloride ($HCl_{(g)}$) and substantial nitric acid decomposition resulting in evolution of gaseous nitrogen oxides.

The main problem of leaching with Aqua Regia is the loss of the volatile source of chloride ions, namely gaseous hydrogen chloride, which are essential for the formation of soluble platinum group metal complex ions in solution.

This loss of chloride ions is detrimental to the leaching efficiency in a number of ways.
Namely :

1. Reduction in leaching rate.
2. Considerable reduction in the degree of recovery of the more "refractory" platinum group metal such as rhodium. Owing to the relative slowness of chlorocomplex formation.
3. The process requires specialized installation of equipment for the absorption of the toxic gaseous products of the decomposition of the reagent.
4. The process requires for the leaching to be carried out in a hermetically closed reactor, often under conditions of elevated pressure.

As a result of these conditions, Aqua Regia leaching is an extremely costly procedure which does not readily result in an acceptably high recovery of platinum group metals.

Most often a total dissolution is not achieved, only a partial separation between the primary and secondary platinum group metals result. This partial separation is only achieved at the cost of leaving a substantial amount of primary platinum group metals undissolved within the gangue material.⁽⁹⁾ Further recovery is often necessary.

For the alternative process proposed, an acid-chloride leach under oxidizing conditions is used for the extraction of platinum, palladium and rhodium. That is, an Aqua Regia based system is used as the leach reagent. However part of the hydrochloric acid component of the leach reagent is replaced/substituted by the dissolved metal chloride salt. This dissolved metal chloride salt, together with the remaining hydrochloric acid portion, acted as the source of chloride ions which are essential for the dissolution of the platinum group metals.

This substitution would more importantly provide for a reduction in the amount of gaseous hydrogen chloride, and hence reduce chloride loss which results in the reduction of the leaching rate associated with the use of Aqua Regia. Also, at high concentrations of dissolved metal chloride salt, it is possible to operate the leaching at temperatures much higher than that possible under normal Aqua Regia conditions.

A similar type of system was proposed and successfully used for the extraction of platinum group metals from scrapped pellet and honeycomb automotive catalysts.⁽¹⁰⁻¹²⁾

Also, current research concerning the partial replacement of hydrochloric acid by less volatile, soluble metal chloride salts, conducted in the Department of Metallurgy at the University of the Witwatersrand has indicated their effectiveness as a chloride ion source for precious metal leaching.

Figure 1 : Pyrometallurgical Process

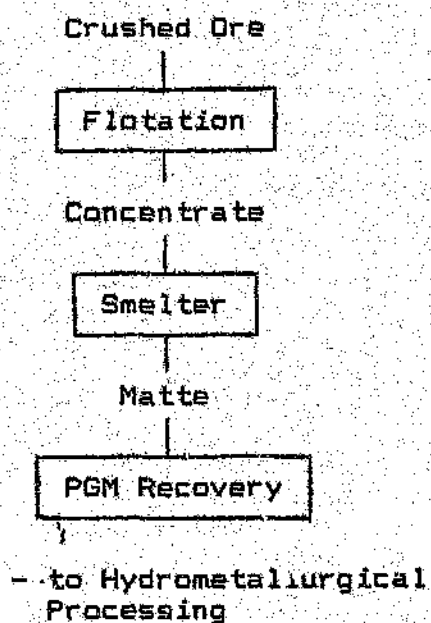
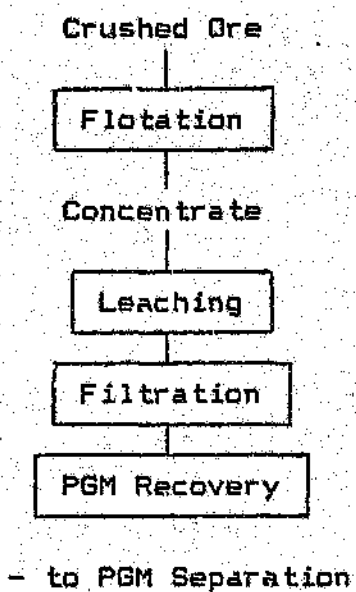


Figure 2 : Hydrometallurgical Process



Platinum Group Metal Chemistry

The six members of the platinum group, ruthenium, rhodium, palladium, osmium, iridium and platinum exhibit distinctive properties including resistance to chemical attack, excellent high temperature characteristics, the ability to catalyze chemical reactions and stable electrical properties.

Insight into their characteristics can be obtained by examining their position in the periodic table.

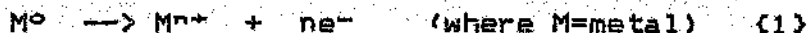
Platinum Group Metals are the second and third triad of group VIII or transition group. The platinum metals in the two triads differ markedly in atomic weight, that is, the second triad is nearly twice as heavy as the corresponding element of the first triad. However, the physical and chemical properties of each metal are very similar to those of the corresponding member in the other triad. For example, platinum and palladium are similar in ductility and chemical properties. Similarly iridium and rhodium, and osmium and ruthenium can be coupled together. (14)

As members to the transition element series they display all the properties associated with transition metals. Various schemes for the grouping the platinum group metal include melting point and atomic weight have been proposed. (15-18)

Platinum group metals have a versatile and complex chemistry. Their nobility is shared to a large degree with both gold and silver, and it refers to the reluctance to dissolve in media that will corrode any base-metal.

A combination of kinetic and thermodynamic factors are involved as follows (9):

(a) The high potential of the reaction



(b) The tendency of the metal, when oxidized, to form a kinetically inert layer of oxide (or chloride) at its surface, and

(c) The inherently slow kinetics of the reaction in (1).

The last two factors operate strongly in the case of the rhodium (Rh).

Generally it dissolves much more slowly in a chloride medium than the primary platinum group metals, platinum (Pt) and palladium (Pd).

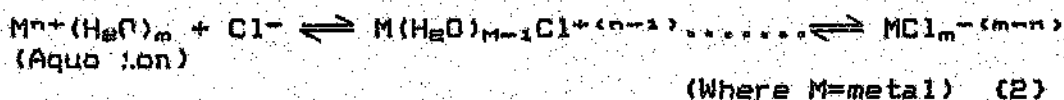
The range of oxidation states (0 to +8) shown by the platinum group metals in an aqueous media is far greater than that found in other transition elements, and their stability of the higher oxidation states is greater. However, this relative stability of these states depends to a large extent on the complexing ligands in the solution.

It is the manipulation of the oxidation states that is one of the most important techniques used for the separation of the platinum group metals.

Platinum, Palladium and Rhodium Chlorocomplexes

Chloride complexing will be important only under high oxidizing and acidic conditions. In solutions where $\text{Cl}^- > 0\text{M}$, the predominant chloride complexes of platinum and palladium will be PtCl_4^{2-} and PdCl_4^{2-} in the temperature range of 25°C to at least 300°C.⁽¹⁹⁾

For chloride media, the chemistry of the aquo ions are insignificant except in the case of Rh(III). Usually there are several species present in equilibrium with one another and can be represented by the general equation⁽²⁾ :



The position of the equilibrium depends on the oxidation state, however for Pd and Pt the equilibrium is almost always completely in favor of the chlorocomplex under acidic conditions.

The situation, however is more complicated for the secondary platinum group metal, Rh(III) which usually exists as mixed complexes.

Chloride ions form relatively strong complexes with Rh^{3+} , but the unusually slow kinetics involved have lead to some questionable estimates of their stabilities. Kinetic studies on both the forward and reverse reaction,

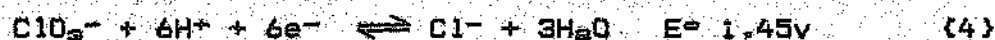
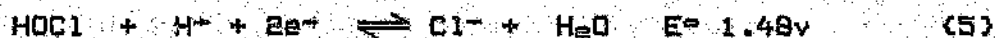
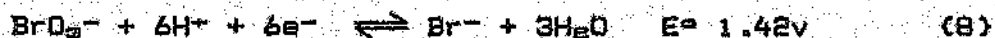


have provided the most reliable estimates of the equilibrium for Rh(III).⁽²⁰⁾

The platinum group metals Pt, Pd and Rh are, in general, very resistant to acid dissolution. Only a very strong hydrochloric acid solution is able to slowly dissolve them under non-oxidizing conditions. However, the presence of a suitable oxidant strongly promotes their dissolution.

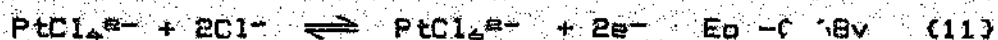
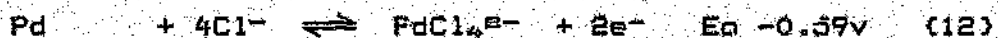
Based on this, almost all process chemistry of platinum group metals involve the use of chlorides plus oxidant.

All of the oxidants below are capable of oxidizing platinum group metals and can theoretically be utilized for their recovery. Standard reduction potentials of commonly used oxidants are as follows (2):



Redox Reactions For Platinum, Palladium and Rhodium

The common oxidation states for platinum are II and IV, for palladium II and for rhodium I and III. For their dissolution their standard potentials in aqueous chloride solutions are as follows (21):



The oxidative reactions (10), (12) and (13) are also dissolution reactions while reaction (11) is a redox reaction which occurs in solution.

The PtCl_4^{2-} chloro-complex ion is unstable and can disproportionate to the free metal and the tetravalent complex:



Dissolution of platinum group metals requires a high chloride ion concentration in an acidic solution, together with the presence of a suitable oxidant.

Such conditions exist when Aqua Regia is used as a leaching reagent.

Since the chemistry of Aqua Regia is not fully understood it is difficult to determine which redox reaction(s) and their corresponding standard potential(s) take(s) place in the solution.

It is generally stated that the reduction reactions of nitric acid are as follows (21):



The E° of all three reactions, (15), (16) and (17) indicate that they will be able to dissolve the platinum group metals of platinum, palladium and rhodium.

Platinum Group Element Mineralogy

In a platinum group element deposit, the platinum group metals fall into two categories⁽²⁾;

- (i) discrete platinum group minerals, and
- (ii) those hosted "invisibly" as impurities within other minerals.

Platinum group minerals may be considered as those minerals in which platinum group metals are an essential part of their stoichiometry and definition. For example, cooperite (PtS).

The second group refers to those in which the platinum group metals are hosted as trace elements and are not determinative to the definition of the minerals. For example, pentlandite $\{(Fe,Ni)_9S_8\}$.

About one third of the platinum group minerals can be grouped as metals, alloys and intermetallic compounds of platinum group metals with Sn, Fe, Pb, Hg, Cu and Ni. The remaining platinum group minerals are platinum group metals formed with S, As, Te, Bi and Sb.

Platinum group metals which are found in bedrock lodes mainly exist as platinum minerals.

The platinum elements plus gold, silver and certain base metals serve as cations in combination most often with arsenic and sulfur.

Sperrylite, $PtAs_2$, is the most widely distributed of all the platinum minerals.

(Table 1: Common Platinum And Palladium Minerals)

The most important deposits are related to basic and ultrabasic rocks. Major world occurrences of platinum group metals may be characterized as follows⁽²⁾:

- (1) Platinum-bearing sulfides of copper, nickel-copper or copper-cobalt that are generically related to basic or ultrabasic igneous rocks.
For example: Sudbury district, Ontario, Canada.
- (2) Platinum-bearing nickel-copper ores concentrated in gabbroic and ultrabasic rocks. The platinum minerals occur mainly in sperrylite and cooperite in the sulfides.
For example: Merensky zone of Bushveld Igneous Complex, Transvaal, South Africa.
- (3) Native platinum metals that are disseminated in dunites.
For example: Uralium deposits, USSR.

Table 1 : Common Platinum And Palladium Minerals

Mineral	Formula	Properties	Form	Metal Content
Sperrylite	PtAs ₂	Tin-White Brittle	Cubic	Pt 52-57%
Cooperite	PtS	Steel-Gray Metallic	Tetragonal	Pt 80-86%
Braggite	(Pt,Pd,Ni)S	Steel-Gray Metallic	Tetragonal	Pt 58-60% Pd 16-20% Ni 2-4%
Native Platinum	Pt	Bright-White Metallic	Cubic	Pt 70-90%

Note : Form is crystal Form

The Merensky Reef is bounded by upper and lower chromitites. (Figure 3) (a)

On a macro scale, the distribution of platinum group element values peak in the chromitite layers. However on a micro scale, they are mostly associated with the base-metal sulphides.

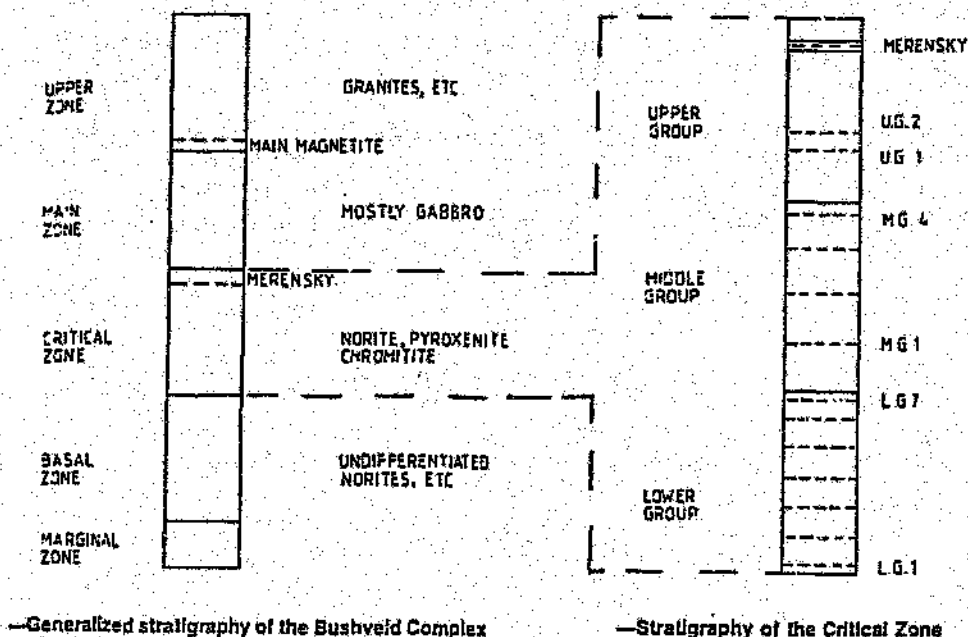
A significant proportion of the platinum group elements can be accounted for by platinum group minerals (45%), although they are mainly (50%) hosted as trace elements in base-metal sulphides.

The major base-metal sulphides are, in order of decreasing abundance, pyrrhotite, pentlandite, chalcopyrite and pyrite.

The platinum group metals are normally found in association with the sulphides as inclusions or along sulphide/silicate grain boundaries. They also occur, to some extent, as inclusions in silicate and in close association with chromite.

It must be noted that the Merensky ore body is remarkably consistent in its composition with the dominant platinum group minerals being cooperite (PtS) and braggite ((Pt,Ni,Pd)S) with subordinate amounts of sperrylite (PtAs₂).

Figure 3 :



Platinum and Chromitite

The association of platinum group metals with the chromitite layer of the Bushveld Complex is well known. (24)

The platinum group metals content and the nature of the platinum group minerals in the UG-2 chromitite layer is as follows (25):

1. The platinum group metals are not distributed evenly throughout the reef.
2. The platinum group metals are predominantly associated with base-metal sulphides or occur close by as discrete minerals enclosed by silicates.
3. The amount of platinum group metals enclosed (occluded) within chromite grains are generally very low. (Less than 12%)
4. The most common platinum group metal enclosed in chromite is laurite, RuS_2 , containing small amounts of iridium and osmium.
5. Considerable lateral variation in platinum group mineralogy of the reef exists.
6. The platinum group metals are extremely small, about $5\mu m$ whilst the associated base-metal sulphides are up to $50\mu m$ in diameter.

The occurrence of most of the platinum group metals between the chromite grains and their association with base-metal sulphides make it possible for these minerals to be liberated by grinding before being concentrated.

Several factors influence the platinum group metal content of tailings.

- (i) Purity of tailings.
A greater separation of chromite and silicate lead to higher platinum group metal content.
(At least double the content)
- (ii) Type of chromium ore.
- (iii) Grain size.
A fine fraction of the tailings result in higher platinum group metal content.
It is believed that the platinum group metals and associated nickel and copper become concentrated in the fine fraction of the tailings during the separation of the chromite.
- (iv) Lateral variations in the platinum group metal content of the layer.

Calculations indicate a resource in the tailings dump of close to 50 000 oz of platinum group metals, with a value of more than R250 million.⁽²²⁾

Clearly, it is evident that an integrated approach in which chromite and platinum group metals are simultaneously extracted could contribute significantly to the profitability of mining the chromite layers in the Bushveld Complex.

No investigation of the platinum group metal content of the LG-6 or main chromitite layer has been done. However, if the information gathered for the MG-1, MG-2 and UG-2 chromitite layers also applies to the LG-6 chromitite layer, then it follows that these platinum group metals should become concentrated in the silicate tailings during the purification of the friable chromite ore with spiral concentrates. Completely liberated platinum group metals and base-metal sulphides, although they have a considerably higher density than the chromite, should also be washed to the silicate tailings because of their minute grain size. The amount of interstitial silicate in LG-6 chromitite layer is approximately 5 to 8%, a pure silicate separation from the chromitite layer should therefore contain more than 5g/t platinum group elements.⁽²²⁾

Pre-Leach Treatment of Concentrates

Roasting

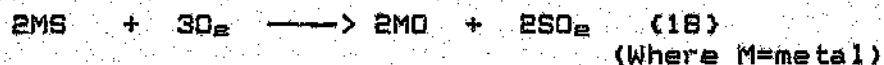
Roasting can be considered as a preparation process because it has the following effects⁽²²⁾:

- (i) Volatilization of impurities that could interfere with the chemistry of metal dissolution, or in the recovery process.
- (ii) Alteration of associated minerals so that they do not enter into the dissolution process.
- (iii) Opening of the mineral structure so that the leach solution can penetrate.
- (iv) Act as a source of leaching reagent.
For example, sulfation to produce sulfuric acid in copper ore leaching.
- (v) Assistance to grinding.
Roasted ores are usually easier to grind.

However, the main disadvantage of roasting a sulphide ore or concentrate is SO_2 production, which is associated with environmental pollution.

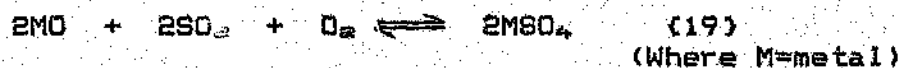
Since all primary deposits of platinum group minerals are usually associated with sulphide ores, the typical reaction for oxidizing sulphide mineral concentrates must be considered.

The generalized reaction can be represented as follows:



However, two other important reactions which also occur during the roasting of sulphides must be considered in addition to reaction (18). These are SO_2 production and metal sulfate production.

Represented generally as:



Both formation and decomposition occur readily, and depend on the temperature of roasting.

Ferrite type compounds are also formed during the roasting process.

Represented by:



It is generally agreed that an oxidizing roast will usually decreases the subsequent dissolution of the secondary platinum group metals, where as a reducing roast improves their leachability.

This effect is possibly related to the formation and removal of refractory oxide layers on the metal surfaces.

Previous research has established that for an oxidative chloride leach, significant improvements in the extraction of platinum resulted when the concentrate was roasted to remove the sulphides prior to chemical leaching.⁽²⁴⁾

Roasting as a pretreatment for gold extraction is also well known.⁽²⁵⁾

Experimental

Leachings of a platinum group metal enriched refractory tailing concentrate were carried out in a stirred glass reactor having the necessary standard instrumentation (Figure 4), to establish if it was possible to use the proposed alternative hydrometallurgical process for the extraction of platinum group metals, specifically platinum, palladium and rhodium.

An acid-chloride leach under oxidizing conditions was used. That is, an Aqua Regia based system was used as the leach reagent. However, part of the hydrochloric acid component of the leach reagent was replaced/substituted by the dissolved metal chloride salt, zinc chloride. This dissolved metal chloride salt, together with the remaining hydrochloric acid portion, acted as the source of chloride ions which are essential for the dissolution of the platinum group metals.

Zinc chloride was utilized as the metal chloride salt, being chosen due to its high solubility in aqueous media and its relative stability at high temperatures. Nitric acid was used as the oxidant.

At high concentrations of dissolved metal chloride salt, it was possible to operate at temperatures which are higher than that of a normal Aqua Regia solution. This high temperature resulted in increasing the overall leaching rate and allowed for the increase in extraction of rhodium to a level which was comparable to both those of platinum and palladium. This increase in the rate of reaction, as a result of the increase in operating temperature, will also provide for a decrease in the size of the reactor. Hence reducing the capital cost associated with plant construction.

Zinc chloride, ZnCl_2 , was used as the metal chloride salt due to its property of being extremely soluble. (22)

ZnCl_2 solubility : 432g per 100g H_2O at 25°C
614g per 100g H_2O at 100°C

Thus allowing for a leaching solution to have a high concentration of chloride ions, which were necessary for the platinum group metal dissolution. The dissolved metal chloride salt, zinc chloride, provided the chloride ions needed for the dissolution of the platinum group metals through the formation of their soluble chlorocomplexes.

The use of a zinc solution also insured that the leach reagent was stable. The pyrohydrolysis reaction of zinc chloride is as follows :



However this only occurs at temperatures of about 124-130°C.

Hence under the chosen leaching conditions of 103°C to 120°C the leach reagent was stable.

A zinc chloride solution is also acidic, pH=1.0 for a 6M solution, which is desired for platinum group metal dissolution. (27)

Various concentrations of zinc chloride in conjunction with nitric acid were tried in order to establish if this type of leaching reagent could be utilized for platinum group metal extraction, without being detrimental to the overall process.

The amount of hydrochloric acid used remained constant in all leachings.

For the extraction of platinum, palladium and rhodium from the tailing concentrate, under an oxidative chloride leach condition, the following reactions can be seen as describing their dissolution.



In the system the use of the metal chloride salt, zinc chloride, provided the chloride ions which are used to form the soluble chloride complexes of platinum (PtCl_6^{2-}), palladium (PdCl_4^{2-}), and rhodium (RhCl_6^{3-}).

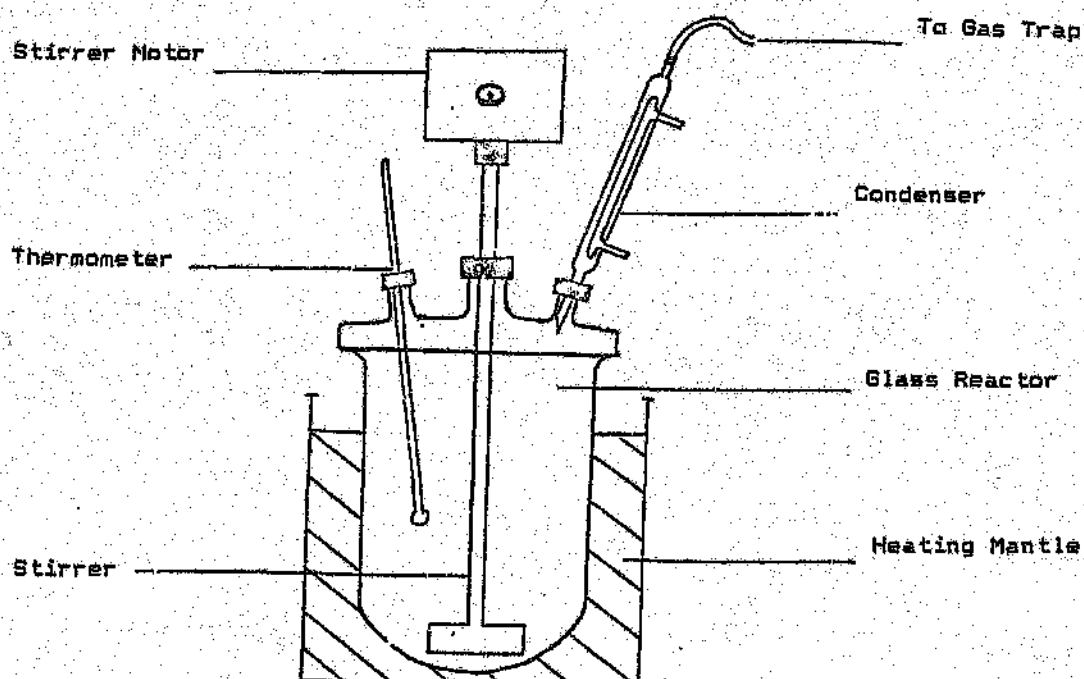
It also provided for free chloride ions in the final solution and provided that the metal chloride concentration was high, it prevented and/or deterred any loss of the platinum group metals from the leach solution through formation of precipitates.

That is, chloride ion concentration in the leach reagent was high therefore ensuring acceptable levels of platinum group metal dissolution, as well as preventing their loss from the solution provided that the acidity of the final solution was relatively low.

Roasting of the concentrate, prior to leaching was also tried to determine if it had any effect on the extraction of platinum group metals, specifically platinum, palladium and rhodium.

Aqua Regia leaching of both the original and the roasted concentrate were carried out for comparison, with the metal chloride based leach reagent.

Figure 4 : Leach Reactor



Aqua Regia Leaching

It is known that a mixture of hydrochloric acid (HCl) and nitric acid (HNO₃), commonly known as Aqua Regia, is an effective leachant of platinum group metals.

Aqua Regia Decomposition

On heating Aqua Regia, an instantaneous and energetic reaction takes place associated with the formation of red-brown fumes.⁽²⁰⁾

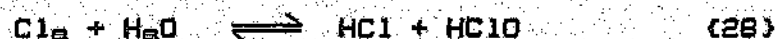
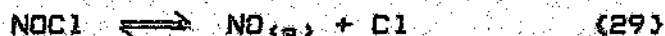
Since there are few specific data on Aqua Regia decomposition, it is difficult to establish the exact decomposition reaction. The following represent a number of reactions that have been proposed for the decomposition of Aqua Regia.⁽²¹⁾



and/or



Side reaction :



Hence depending on which decomposition reaction for Aqua Regia is assumed, the dissolution reactions of platinum group metals can be represented in a number of ways.

Results Of Aqua Regia Leaching

Aqua Regia leaching of the concentrate was carried out in the equipment that was used for the oxidative metal chloride leachings. (Figure 4)
The following extractions were obtained.

Table 2 : Aqua Regia Leaching of Concentrate.

Type of Leach	Percentage Extraction					
	Pt	Pd	Rh	Fe	Ni	Cr
Direct	178.77	186.98	164.13	164.13	197.60	118.22
Roasted	188.27	181.57	178.60	157.53	178.48	113.15

Note : Leach Temperature ca 100°C, Time 2.5hr.
Concentrate roasted at 450°C for 1hr.

Aqua Regia leaching of the concentrate resulted in satisfactory platinum group metal extraction, while leaching of the roasted concentrate lead to an improvement in platinum group metal extraction.
These results can be compared to those achieved when using the zinc chloride/hydrochloric acid/nitric acid leach reagent.

Metal Chloride Leaching

A predetermined amount of zinc chloride, by weight, was dissolved in distilled water to produce the desired concentration of metal chloride solution. Concentrated hydrochloric acid (34%) and concentrated nitric acid (55%) were added to the zinc chloride solution to form the desired leach reagent.

The concentration of hydrochloric acid in all leach reagents was 1.0M, and it provided a proportion of the chloride ions required for the platinum group metal dissolution. The zinc chloride acted as the major chloride ion carrier in the leach reagent.

The reactor was heated, with slow stirring until a temperature of approximately 75°C. At this point the desired amount, by weight, of concentrate was added to the leaching reagent ($\text{ZnCl}_2/\text{HCl}/\text{HNO}_3$). The mixing rate was increased, up to approximately 500rpm, in order to prevent sedimentation of the solid during leaching and thus allow for optimum extraction of platinum, palladium and rhodium. The time of concentrated addition was taken as the zero time for the leach.

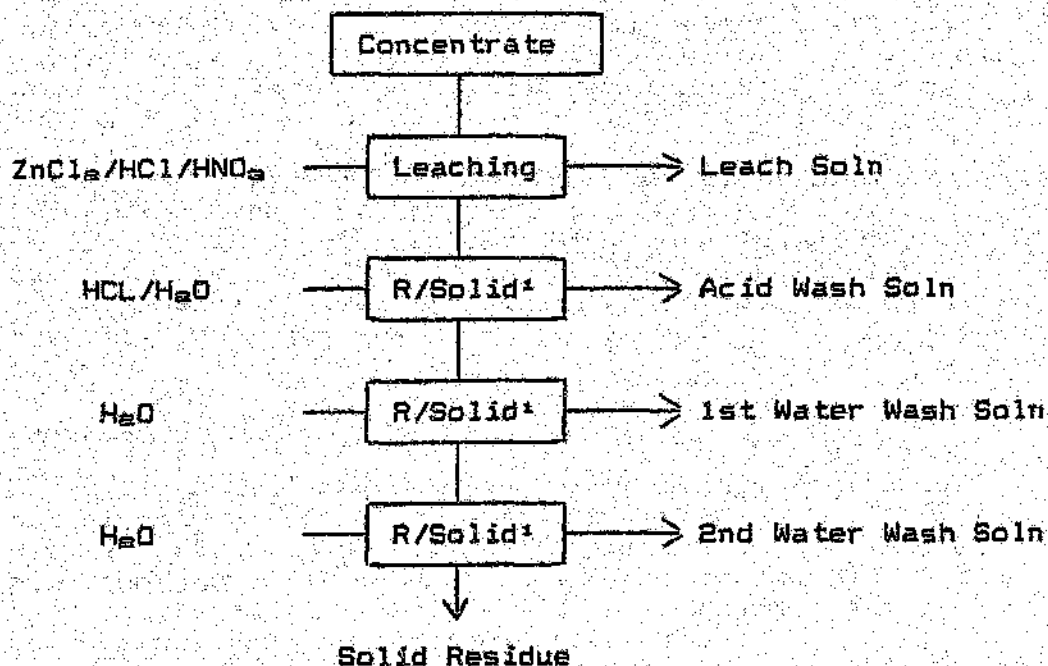
Heating was continued until the leach reagent was boiling. A condensor provided for the return of any evaporated water to the leach solution. Since HCl gas is extremely soluble in water, it would be rapidly dissolved in the condensed water and also be recycled to the reactor. The gas trap was needed for the collection of NO_x , which resulted from the decomposition of the oxidant, nitric acid.

On completion of the leach, both heating and stirring of the reaction mixture were stopped and the reaction mixture allowed to cool. During this period of time sedimentation of the solid occurred, thus limiting any further extraction of the platinum group metals to a minimum. At a temperature of 60°C to 65°C, the reaction mixture was filtered using a buchner vacuum filter. This allowed for a rapid separation of the residual solid and leach solution.

The residual solid was washed, firstly with an acid wash ($\text{HCl}/\text{H}_2\text{O}$ 1:1), then repeatedly with distilled water until the end filtrate had a pH of 4.

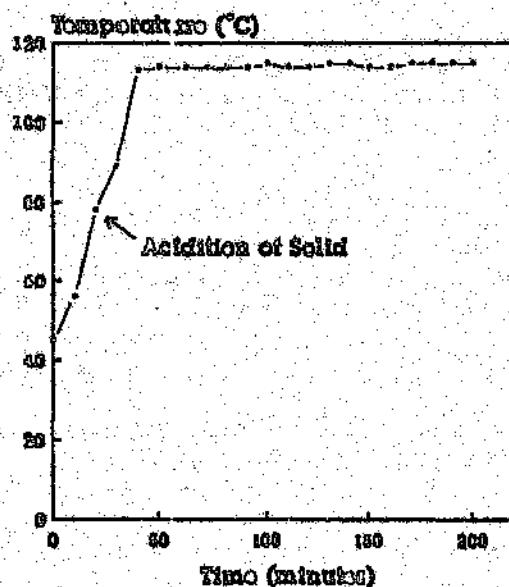
The solid was oven dried, temperature 50°C to 70°C, overnight and a portion taken for digestion.

Figure 5 : Typical Experimental Procedure



Note 1 : R/Solid = Residual Solid

Figure 6
Typical Reaction Profile



Digestion Of Residual Solid

An accurate weight of solid, was digested firstly with concentrated perchloric acid (70%), followed by an Aqua Regia digestion. The resulting solution was sent for analysis together with leach and wash solutions.

This type of digestion procedure was followed in order to ensure that there was complete solubilization of any remaining platinum group metals. Thus allowing for an accurate determination of the degree of platinum, palladium and rhodium extraction which occurred during the oxidative chloride leach.

Analysis

Materials containing platinum group metals are noted to be notoriously difficult to analyze.⁽³¹⁻³⁴⁾

However, because of their high average atomic numbers, platinum group metals are easily detected on a back-scattered electron image of a scanning electron microscope (SEM) or electron microprobe.

The X-ray fluorescence thin-film sample presentation technique has been applied for platinum group metal determination. Combining with fire-assay techniques, the thin-film technique provided a relatively simple analytical method for platinum group metal determination.

Inductively coupled plasma-mass spectrometry (ICP-MS) has limits for determining individual platinum group metals as low as ten nanograms per gram.⁽³⁷⁾

Analysis were carried out by the Council for Mineral Technology (MINTeK), Analytical Science Division.

Solution Analysis :

Concentration of Chromium, Nickel and Iron were determined by ICP-OES, while the platinum group metals, Platinum, Palladium and Rhodium were determined by ICP-MS.

Solid Analysis :

Concentrations of the individual platinum group metals were determined by atomic absorption on the "prill" collected by fire assay in both original concentrate and residual solids.

Chromium, Nickel and Iron were determined by ICP-OES.

Results And Conclusions

1. Effect Of Roasting

a. Weight Loss On Roasting

A systematic increase in the loss of weight of the concentrate occurred as the temperature of roasting increased. (Table 3, Figure 7)

This loss in weight as roasting temperature increased can be attributed to the increase in loss of sulphide through the formation of SO_2 during the roasting procedure. Even though the concentrate was oven dried prior to roasting, the loss of tightly bound water molecules during roasting can not be excluded. Roasting time was 1 to 1.5 hours at the desired temperature.

Table 3 : Effect of Roasting Temperature on Weight Loss.

Roast Temperature (°C)	Weight Loss ¹ Roast (%)	Weight Loss ² Leach (%)
0	0.0	20.76
200	2.0	20.21
450	2.4	18.43
650	3.9	15.62
750	6.6	11.10

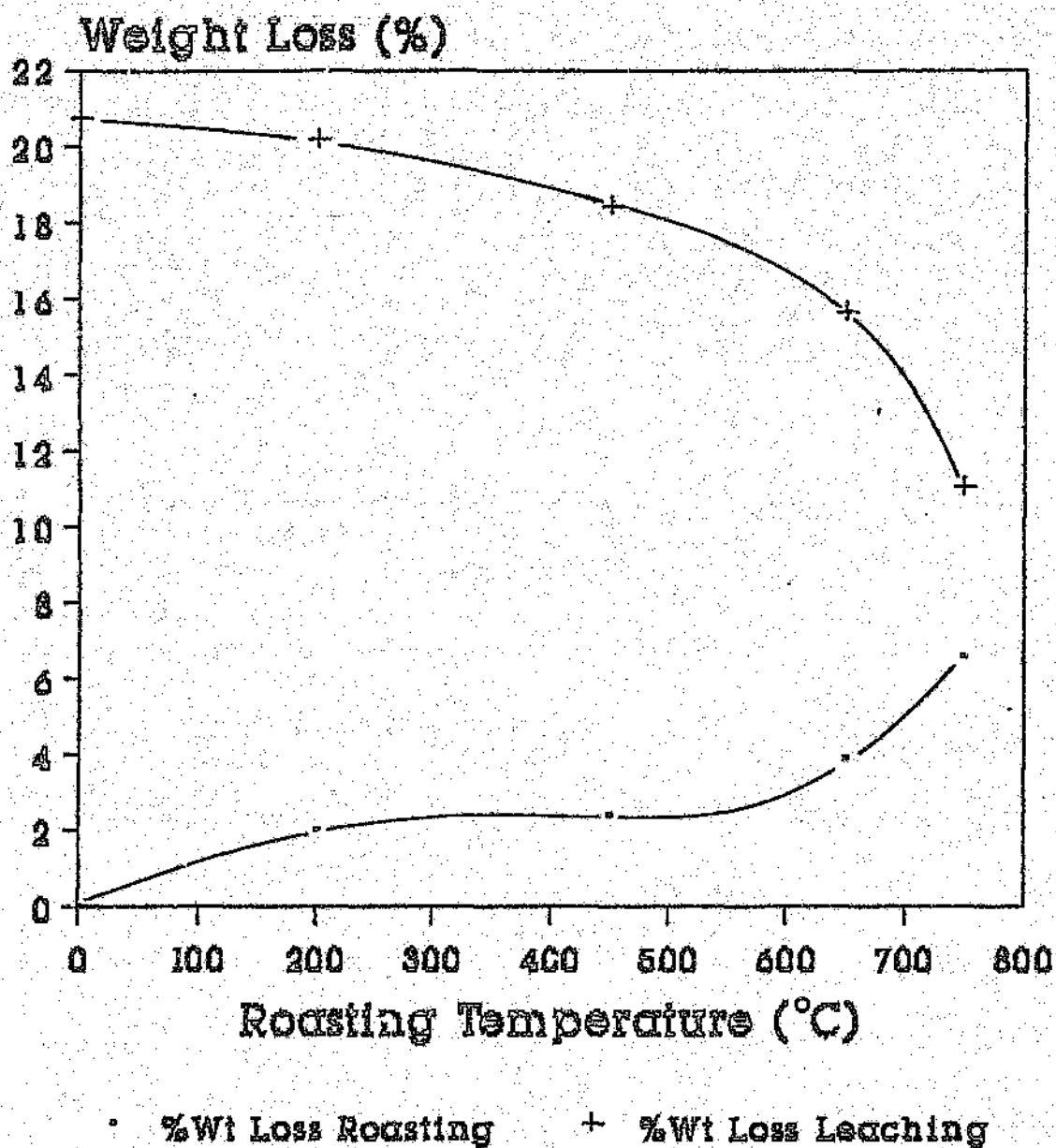
1 - Percentage weight loss during roasting.

2 - Percentage weight loss on subsequent leaching.
Leaching carried out under similar conditions.

The decrease in percentage weight loss during the subsequent leaching of the roasted concentrate can be explained by the formation of insoluble material during the roasting procedure. The higher the roast temperature, the greater the formation of insoluble, non-extractable, material.

This insoluble material probably consists of iron and/or chromium, which both show the trend of decreased extraction as the temperature of roasting was increased.

Figure 7
Roast Temperature Vs Weight Loss



b. Effect Of Roasting On The Degree Of Extraction

Roasting of the concentrate prior to the oxidative chloride leaching proved to be beneficial for the extraction of platinum group metals, especially in the case of platinum. (Table 4)

Table 4 : Roasting Temperature Vs Degree Of Extraction.

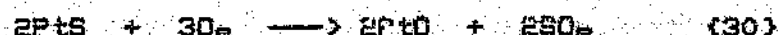
Roast Temperature (°C)	Percentage Extraction					
	Pt	Pd	Rh	Fe	Ni	Cr
0	171.3	179.3	163.9	159.6	187.1	111.2
200	171.6	182.1	163.0	161.5	191.1	121.1
450	183.0	173.5	166.3	151.2	195.3	16.6
650	193.4	175.0	182.9	146.1	189.2	8.3
750	189.1	188.2	168.0	145.3	186.3	8.7

Note : leaching carried out under similar conditions.
 [ZnCl₂] 3.6729M; HNO₃ 10-12.5% (wt/vol)
 leach temperature 103-105°C; Time 2.5-3hr
 Liquid/solid ratio 3.9-4.7 (ml/g).

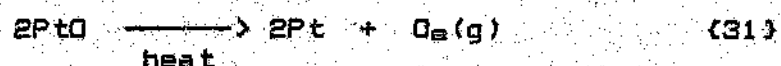
This improvement in the degree of platinum extraction can be explained in two ways.

The roasting of the concentrate, prior to the oxidative chloride leach resulted in the removal of sulphide thereby creating a more readily accessible platinum complex for dissolution.

That is, the formation of the platinum oxide, PtO.

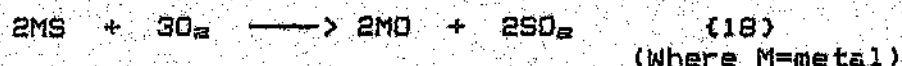


On heating, that is under roasting conditions, the formed platinum oxide, PtO dissociated, thus liberating the platinum and thereby making it more available for extraction though the formation of its soluble chlorocomplex.



However, if the platinum was not in the form, PtS, in the concentrate the reaction (30) above would not take place during the roasting.

However, since the concentrate was a sulphidic mineral concentrate, the general type of reaction that will occur during the roasting procedure would be :



This type of reaction would cause an opening of the mineral structure, thereby resulting in a greater penetration of the leach reagent. This increase in accessibility of the leach solution towards the platinum group metals, especially platinum, would result in a greater extraction from the roasted concentrate.

Either one or both conditions would therefore have resulted in an increase in the dissolution and hence increased the degree of extraction of platinum from the roasted concentrate on its subsequent oxidative chloride leach.

The relationship between the roasting temperature and the degree of platinum group metal extraction, particularly for platinum, indicated that a temperature of 450°C and above results in an improved extraction.

If the oxide, PtO, was formed during the roasting it would only dissociate to the free metal at temperatures greater than 200°C. (28)

This can explain why there was no improvement in the degree of platinum extraction during the subsequent leaching of the concentrate which was roasted at 200°C.

The apparent decrease in palladium extraction in relation to the roasting temperature is possibly explained by the formation of the palladium oxide, PdO, during roasting. The oxide, PdO is insoluble under acidic conditions and only dissociated to the free metal at a temperature of 875°C. (28)

Since the maximum roasting temperature used was 750°C, the dissociation of PdO would therefore not have taken place. Hence the decrease in the degree of extraction observed.

The formation of the metal oxide, MO and loss of SO_2 during roasting is supported by the fact that, when roasting of the concentrate was performed under conditions of reduced oxygen concentration, at 650°C , the extraction of platinum group metals by the subsequent oxidative chloride leach gave results which were comparable to those found during the direct leaching of the concentrate. For example: Platinum extraction was 68.9%.

That is, under conditions of reduced oxygen content roasting, the formation of oxides and loss of SO_2 is inhibited. This resulted in a situation which could be compared to the use of a non-roasted concentrate.

The above result clearly indicated that the formation of the metal oxide, MO, during the roasting procedure was the cause of the enhanced platinum extraction rather than that of a simple fracturation of the minerals within the concentrate, which could have occurred as a result of high temperatures.

From the results (Table 4), it is evident that there was a decrease in iron extraction as the roasting temperature increased.

This decrease as roast temperature increased can be explained as follows.

The iron oxide, Fe_2O_3 , can be formed by heating iron(II) sulphate, iron(II) oxide and roasting iron(II) disulphide (pyrites) in air or oxygen.⁽³⁹⁾

Even though, Fe_2O_3 is essentially basic it reacts only slowly with acids.

Thus as the roasting temperature increased, there would be greater formation of Fe_2O_3 . This would result in the lowering of iron extraction due to the much reduced dissolution of Fe_2O_3 in the acidic leach reagent.

For Nickel extraction, the results (Table 4) indicated that there was an apparent optimum extraction at a roasting temperature of 450°C .

This optimum in the extraction of nickel at a roast temperature of 450°C was also established by Shukla⁽⁴⁰⁾, who stated that "for good nickel recovery from a sulphide concentrate the optimum roasting temperature was between 450°C and 500°C for acid leaching."

Reid⁽⁴¹⁾ found a similar result.

From the results discussed, it is clearly evident that the main minerals in the concentrate are most likely to be cooperite (PtS) and braggite ((Pt,Pd,Ni)S), since the result of the reduced oxygen content roasting lead to a degree of extraction of platinum, palladium and rhodium which were comparable with those established for leaching of the unroasted concentrate. This is consistent with the source of concentrate being the Merensky Reef.

2. Effect Of Metal Chloride Concentration On Extraction

The density of an aqueous zinc chloride solution can be used as an indicator to its concentration.

Hence by measuring the density, one could readily determine the concentration of the various zinc chloride solutions which were utilized for the leaching of the concentrate. (Table 5, Figure 8)

In this way the effect of concentration of the zinc chloride based leach solution on the degree of extraction was determined.

Table 5 : Relationship Between Density And Concentration For Zinc Chloride Solutions.

For 20°C		For 60°C	
Density ¹	[ZnCl ₂] ²	Density ¹	[ZnCl ₂] ²
1.24	1.25	1.235	2.50
1.29	1.85	1.350	3.45
1.36	2.60	1.410	4.10
1.43	3.40	1.495	4.90
1.47	3.75	1.570	5.75
1.53	4.45	1.655	6.70
1.59	5.10		
1.61	5.35		

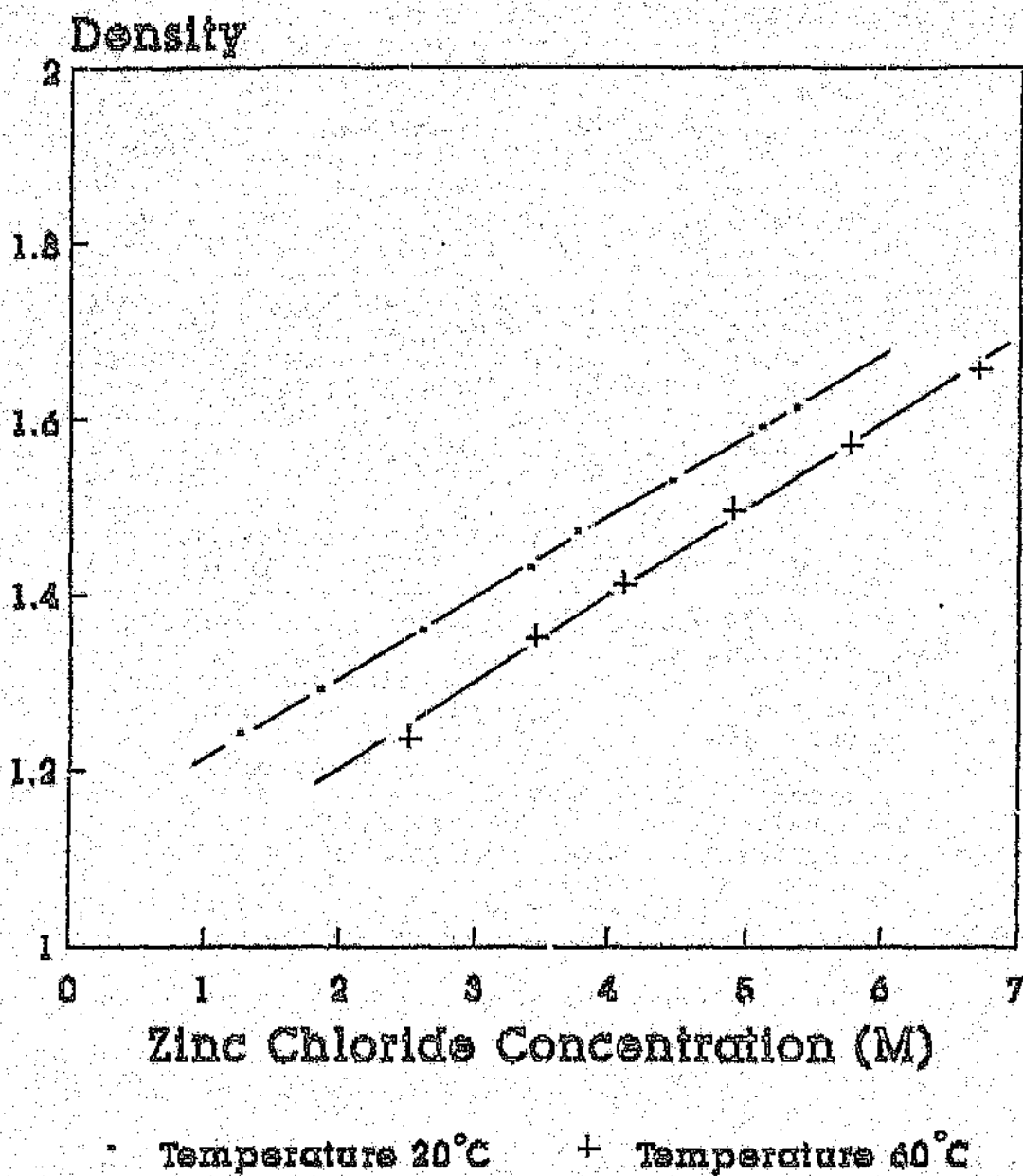
1 - Density of ZnCl₂(aq) g/cm³.

2 - Concentration of ZnCl₂ M.

However, it must be noted that the density of the zinc chloride solution is dependent on the solution temperature. Consequently all density determinations had to be done at the same temperature in order to achieve a correct value for the concentration of the zinc chloride solutions used for the leaching.

All density measurements were done at room temperature.

Figure 8
Zinc Chloride Concentration Vs Density



2. Effect Of Metal Chloride Concentration On Extraction

a. Direct Leaching Of Concentrate

Direct leaching of the concentrate using the leach reagent, zinc chloride(aq)/hydrochloric acid/nitric acid resulted in the following extractions.
(Table 6, Figures 9-12)

Table 6 : Effect of Zinc Chloride Concentration on Extraction.

Density g/cm ³	Percentage Extraction						% Weight Loss ¹
	Pt	Pd	Rh	Ni	Fe	Cr	
1.290	177.0	81.2	61.6	95.7	54.6	1.4	8.47
1.292	185.9	86.3	67.7	72.3	43.3	11.4	20.14
1.359	153.9	82.8	61.4	94.3	61.9	17.1	20.94
1.368	180.7	81.2	65.7	89.1	60.4	14.2	20.53
1.376	179.2	49.0	65.2	96.2	59.3	16.6	22.29
1.391	168.3	68.9	52.8	96.7	56.5	5.4	23.42
1.396	180.0	79.9	63.5	97.4	61.7	12.7	23.40
1.411	179.4	74.0	64.5	77.8	56.6	2.2	20.83
1.420	178.6	84.2	63.3	97.6	64.4	17.6	28.18
1.495	164.4	78.6	67.6	96.8	72.3	51.8	19.45

Note : 1 - Percentage Weight loss on leaching.

2 - Erroneous results - due to analysis problems. PGM analysis is difficult particularly when the concentrations are low. The presents of Cr can also lead to erroneous results due to interference.

All leaching were carried out under similar conditions. Nitric acid 9.99-20.81% (wt/vol); Temperature 102°C-110°C Time 2.5-3hr; Liquid/Solid ratio 3.55-6.9 (ml/g).

The distribution of results is primarily due to the fact that the concentrations within the refractory concentrate were low. Particularly for platinum, palladium and rhodium.

Average extractions excluding the erroneous results are :

Platinum (Pt) 78.64%

Palladium (Pd) 81.03%

Rhodium (Rh) 64.50%

Nickel (Ni) 95.47%

Iron (Fe) 59.42%

Chromium (Cr) 14.93%

Average percentage weight loss on leaching : 22.13%

Figure 9
Density Vs % Extraction
Direct Leaching

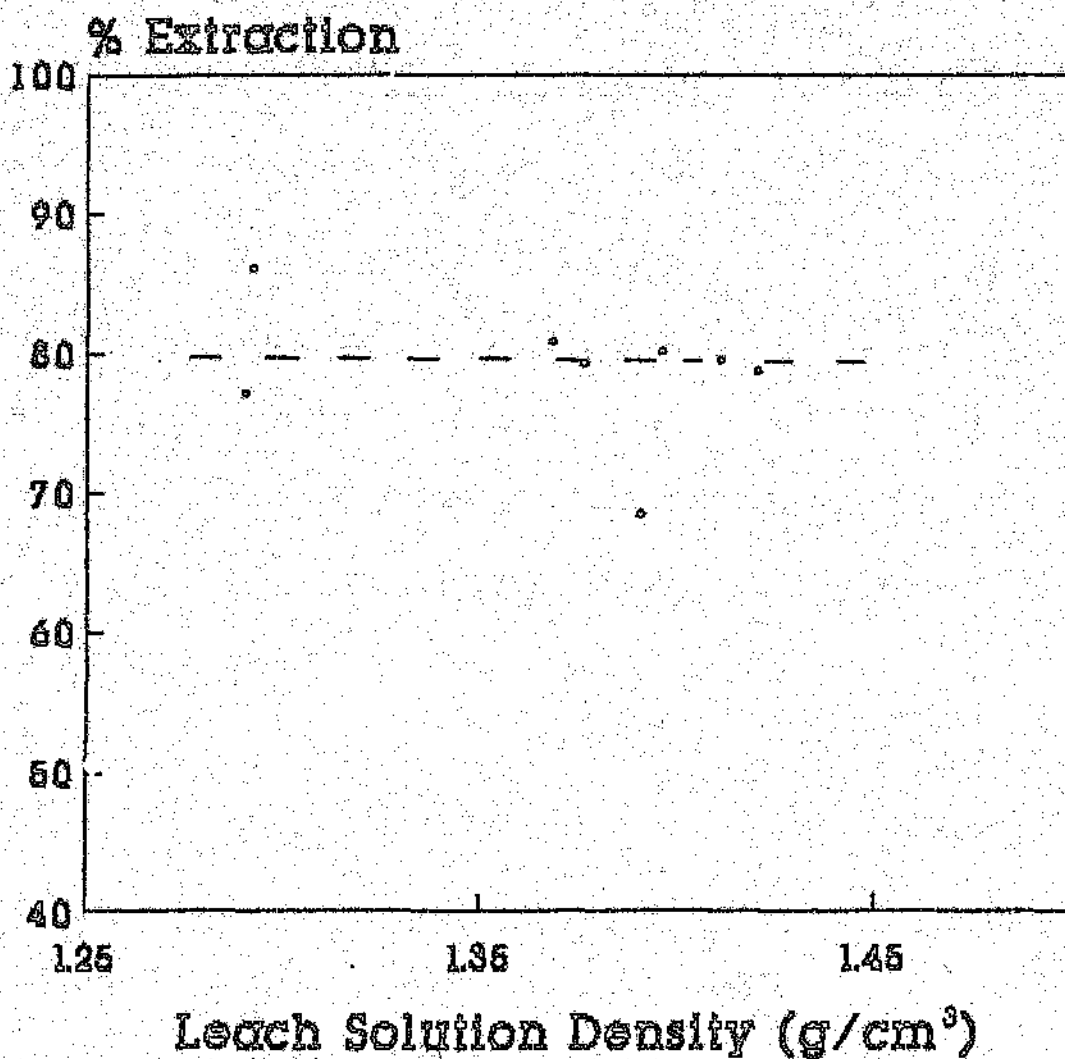
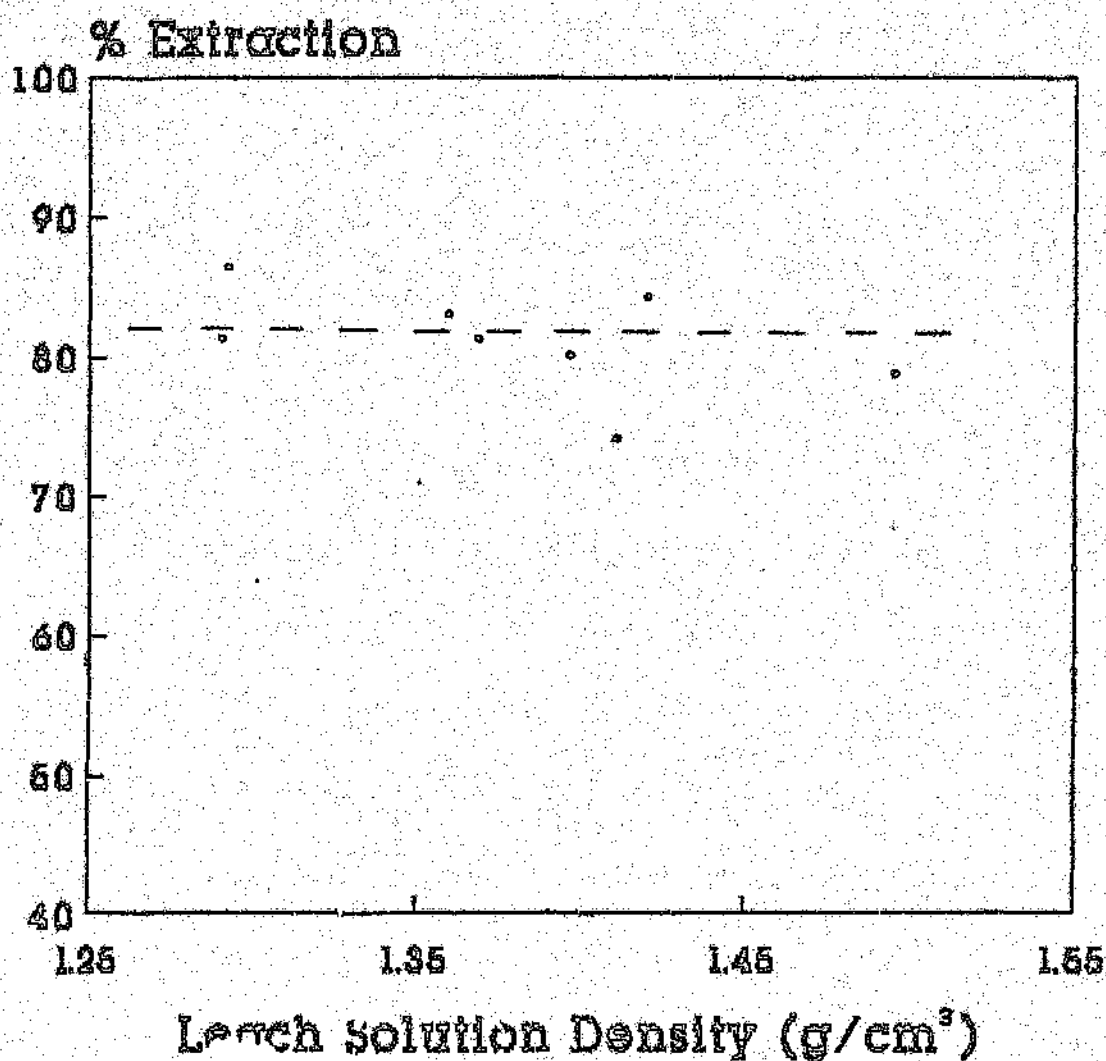


Figure 10
Density Vs % Extraction
Direct Leaching



• Palladium (Pd)

Figure 11
Density Vs % Extraction
Direct Leaching

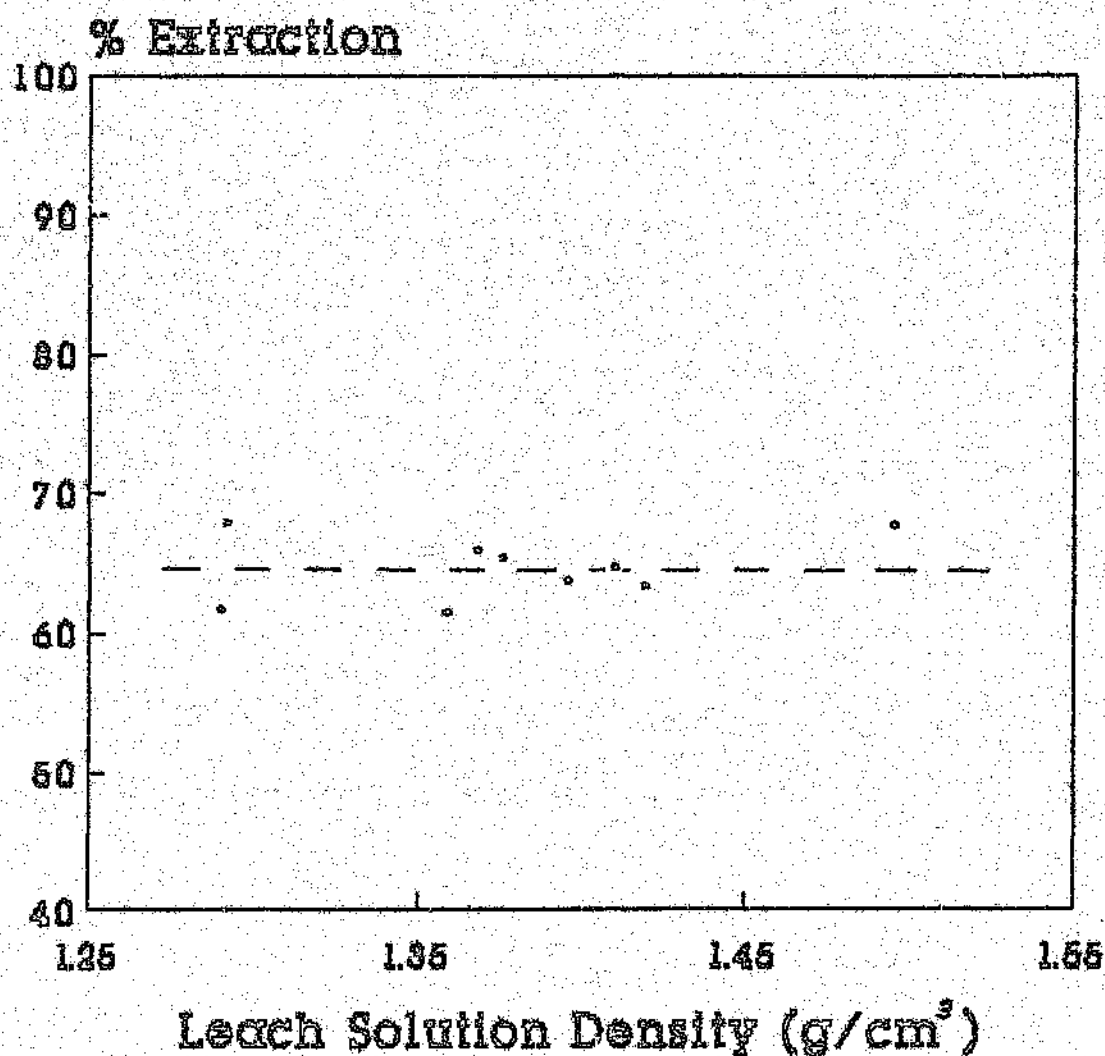
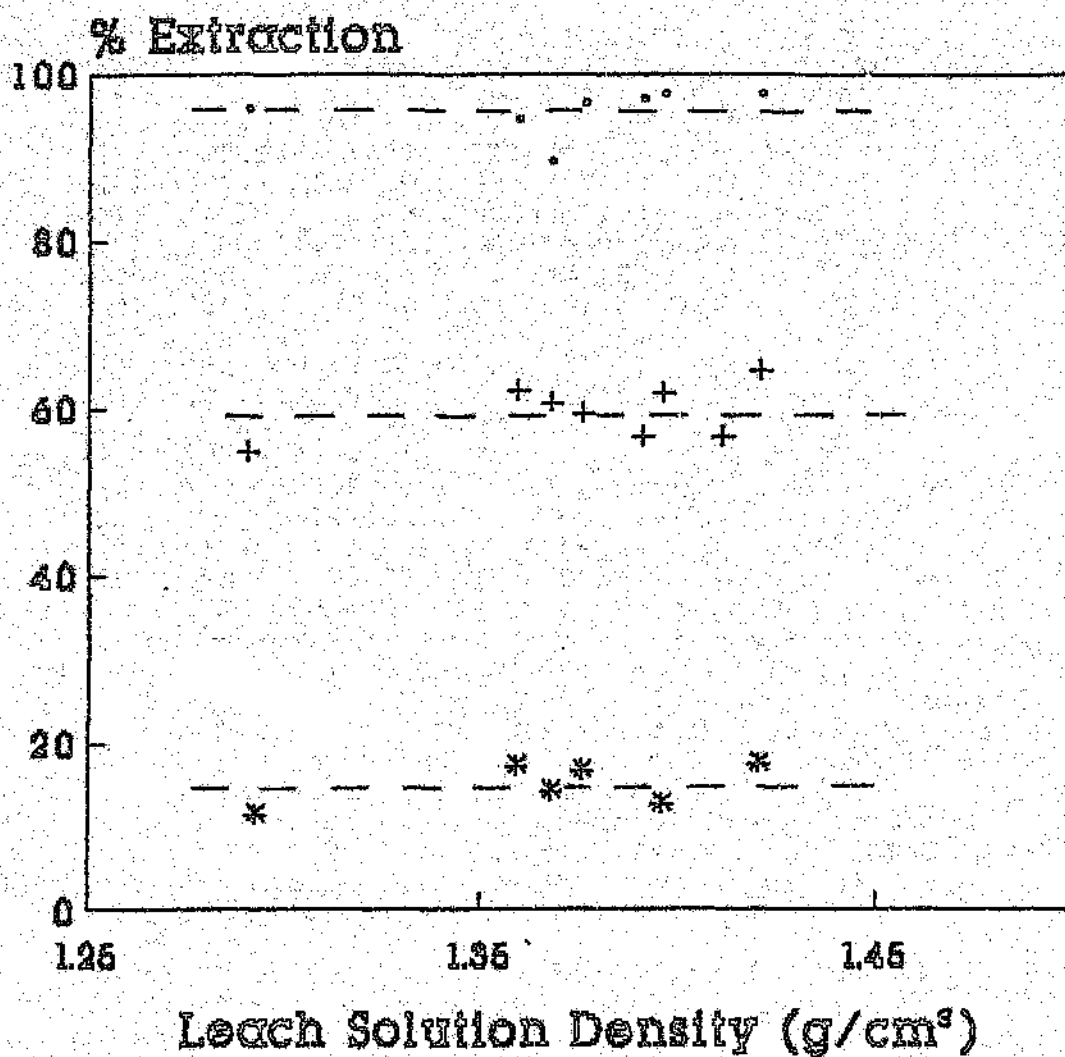


Figure 12
Density Vs % Extraction
Direct Leaching



• Nickel (Ni) + Iron (Fe) * Chromium (Cr)

2. Effect Of Metal Chloride Concentration On Extraction

b. Leaching of Roasted Concentrate

Leaching of a roasted concentrate using the leach reagent, zinc chloride(aq)/hydrochloric acid/nitric acid resulted in the following extractions. (Table 7, Figures 13-18)

Table 7 : Effect of Zinc Chloride Concentration on Extraction.

Density	Percentage Extraction							% Weight
g/cm ³	Pt	Pd	Rh	Ni	Fe	Cr	Loss ¹	
1.312	185.9	186.3	167.7	172.3	143.3	11.4	12.81	
1.321	194.1	181.5	188.5	188.8	146.2	6.0	18.89	
1.391	195.4	180.2	186.5	192.4	150.5	3.4	20.00	
1.405	193.6	171.7	189.0	188.3	145.1	7.4	17.41	
1.410	183.0	173.5	166.3	195.3	151.3	6.6	18.43	
1.431	189.1	188.2	168.0	186.3	145.3	8.7	11.10	
1.449	189.4	177.6	175.5	185.6	141.9	8.7	16.89	
1.452	192.8	180.1	183.0	193.9	151.5	---	20.50	
1.465	186.3	172.3	181.1	181.0	140.0	14.3	14.50	
1.468	193.4	175.0	182.9	189.2	146.1	8.3	15.62	
1.494	193.9	177.1	159.9	174.9	126.1	3.1	11.55	
1.516	188.1	185.7	180.4	179.4	155.1	140.7	14.90	
1.520	182.9	183.9	184.3	179.7	145.8	14.2	10.46	
1.570	197.1	189.0	190.0	188.9	144.7	5.3	16.67	
1.610	188.7	176.9	177.4	192.5	151.2	6.6	17.33	
1.620	192.0	172.4	181.2	176.5	129.8	1.7	12.00	

Note : 1 - Percentage Weight loss on leaching.

2 - Erroneous results - due to analysis problems.

PGM analysis is difficult particularly when the concentrations are low. The presents of Cr can also lead to interference.

All leaching were carried out under similar conditions.

Nitric acid 9.99-24.97% (wt/vol); Temperature 103°C-123°C

Time 1.5-3hr; Liquid/Solid ratio 3.64-6.9 (ml/g).

Concentrate roasted at 650°C for 1hr.

The distribution of results is primarily due to the fact that the concentrations within the refractory concentrate were low.

Particularly for platinum, palladium and rhodium.

Average extractions excluding the erroneous results are :

Platinum (Pt) 90.85%

Palladium (Pd) 79.46%

Rhodium (Rh) 80.12%

Nickel (Ni) 85.31%

Iron (Fe) 47.54%

Chromium (Cr) 8.86%

Average percentage weight loss on leaching : 15.57%

Figure 13
Density Vs % Extraction
Roasted Concentrate

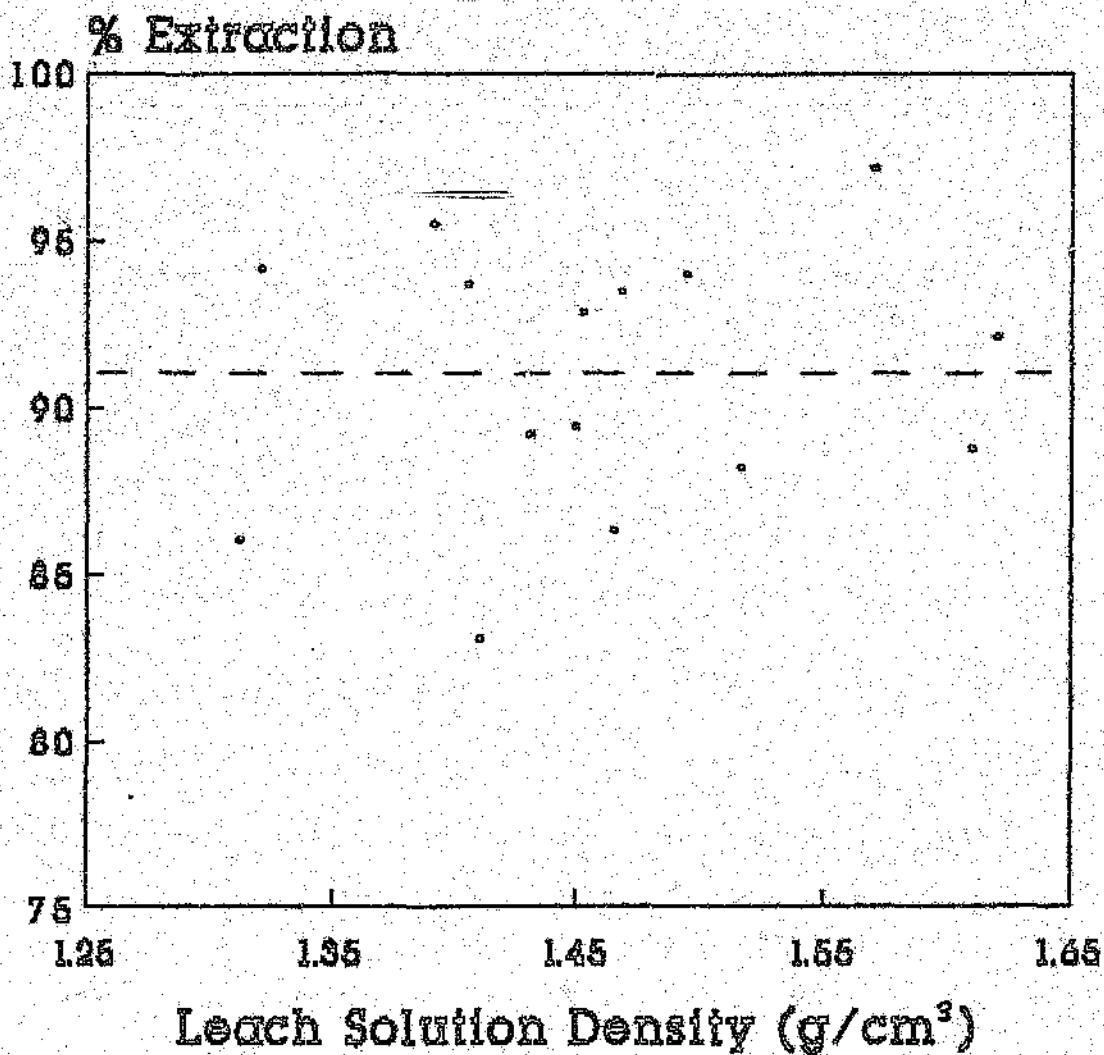
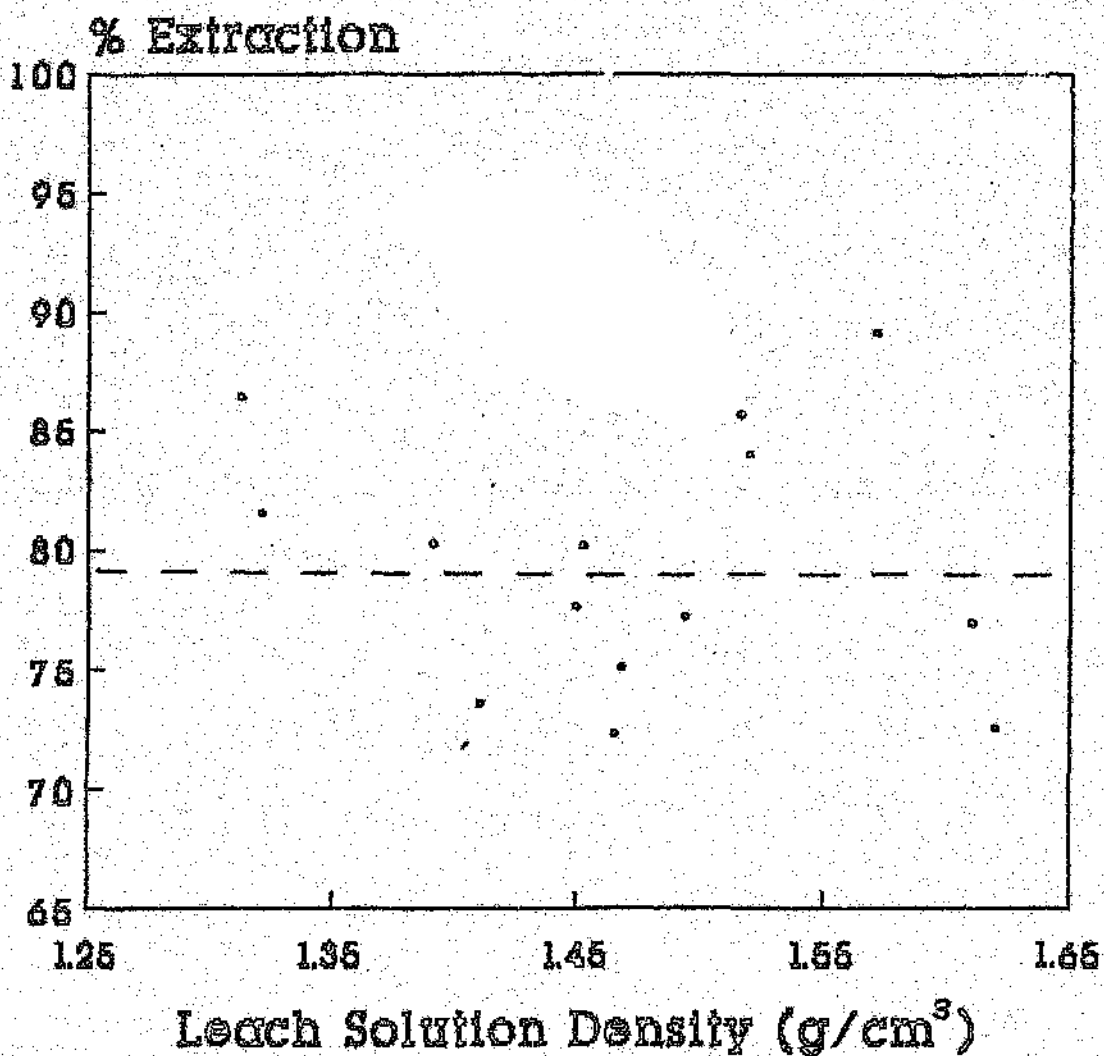
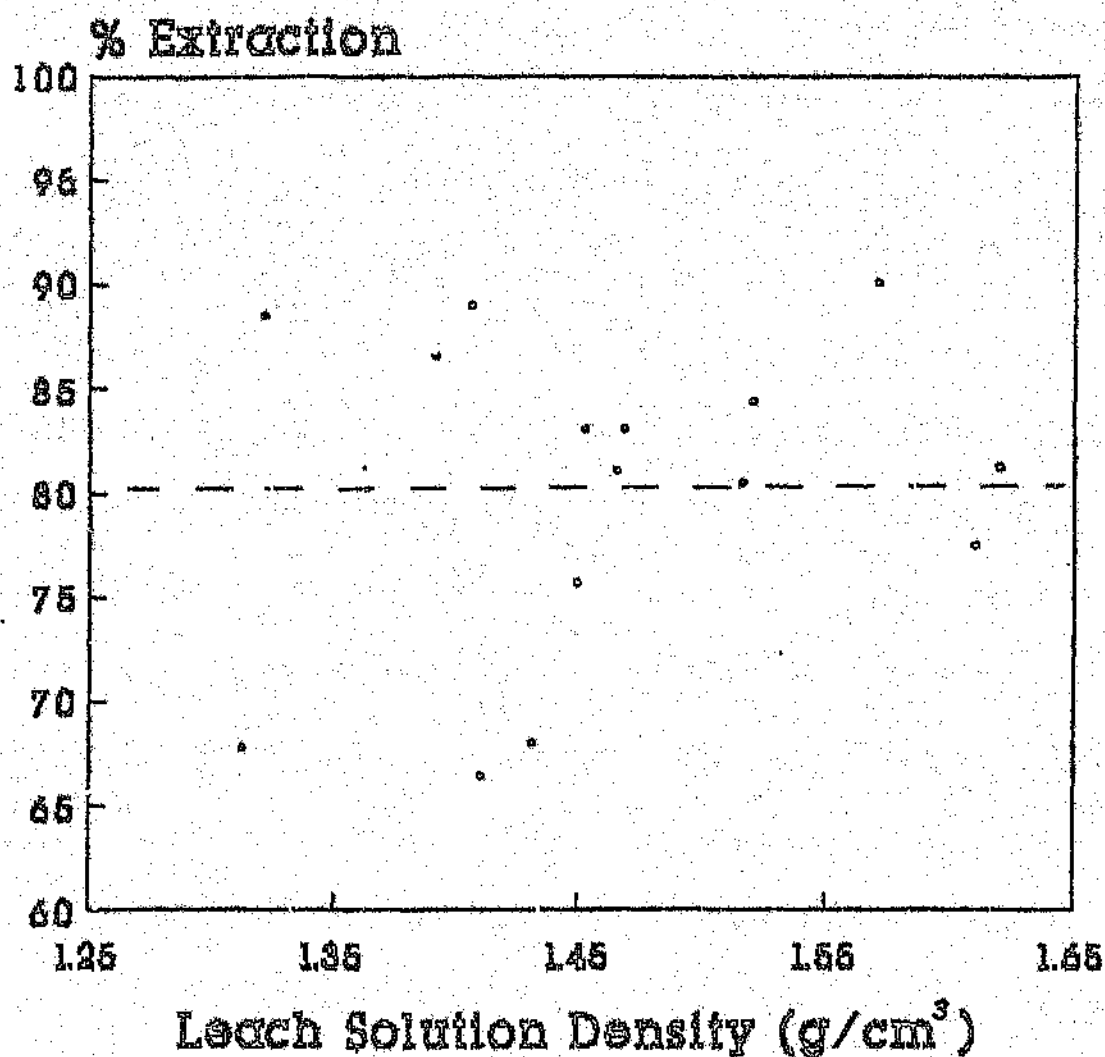


Figure 14
Density Vs % Extraction
Roasted Concentrate



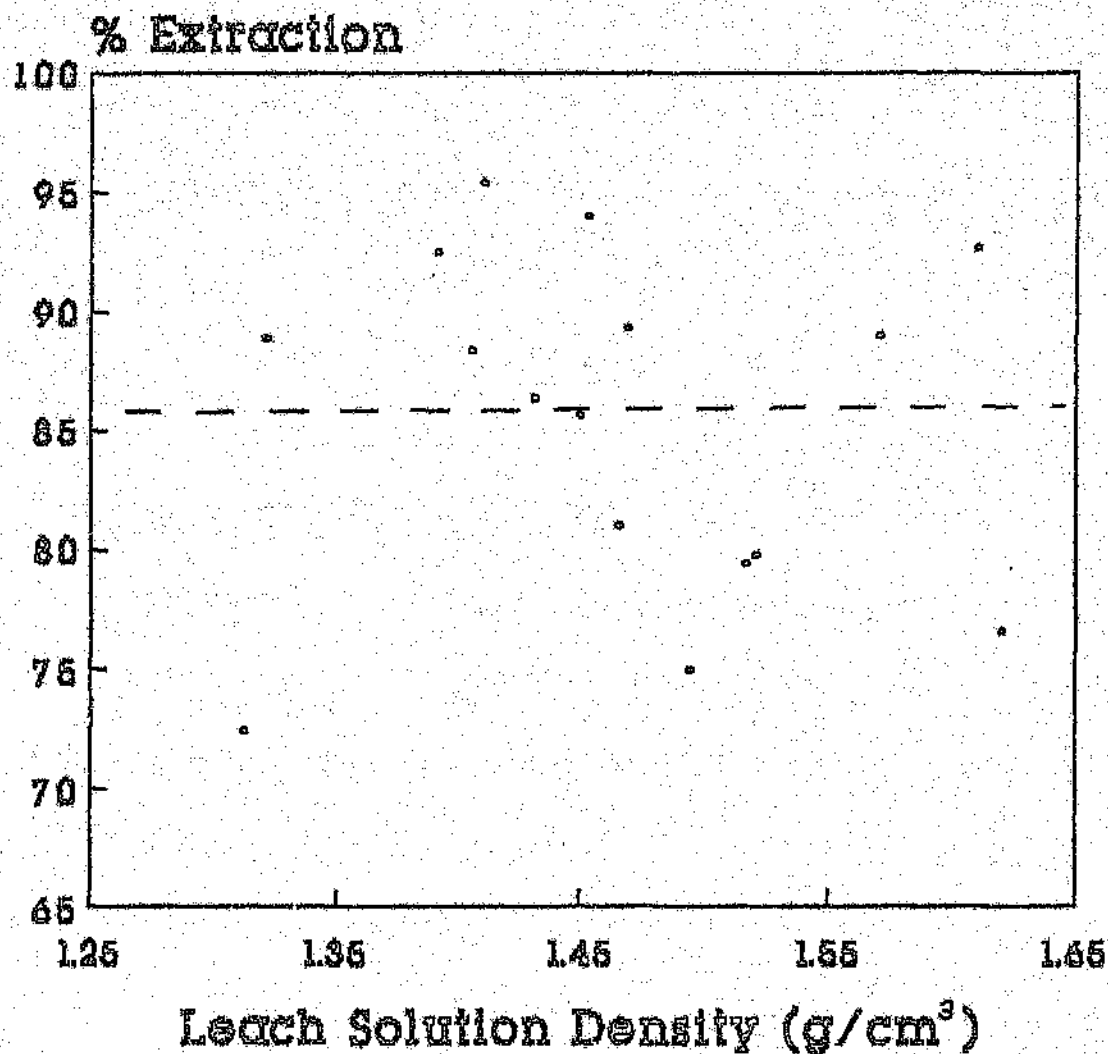
Palladium (Pd)

Figure 15
Density Vs % Extraction
Roasted Concentrate



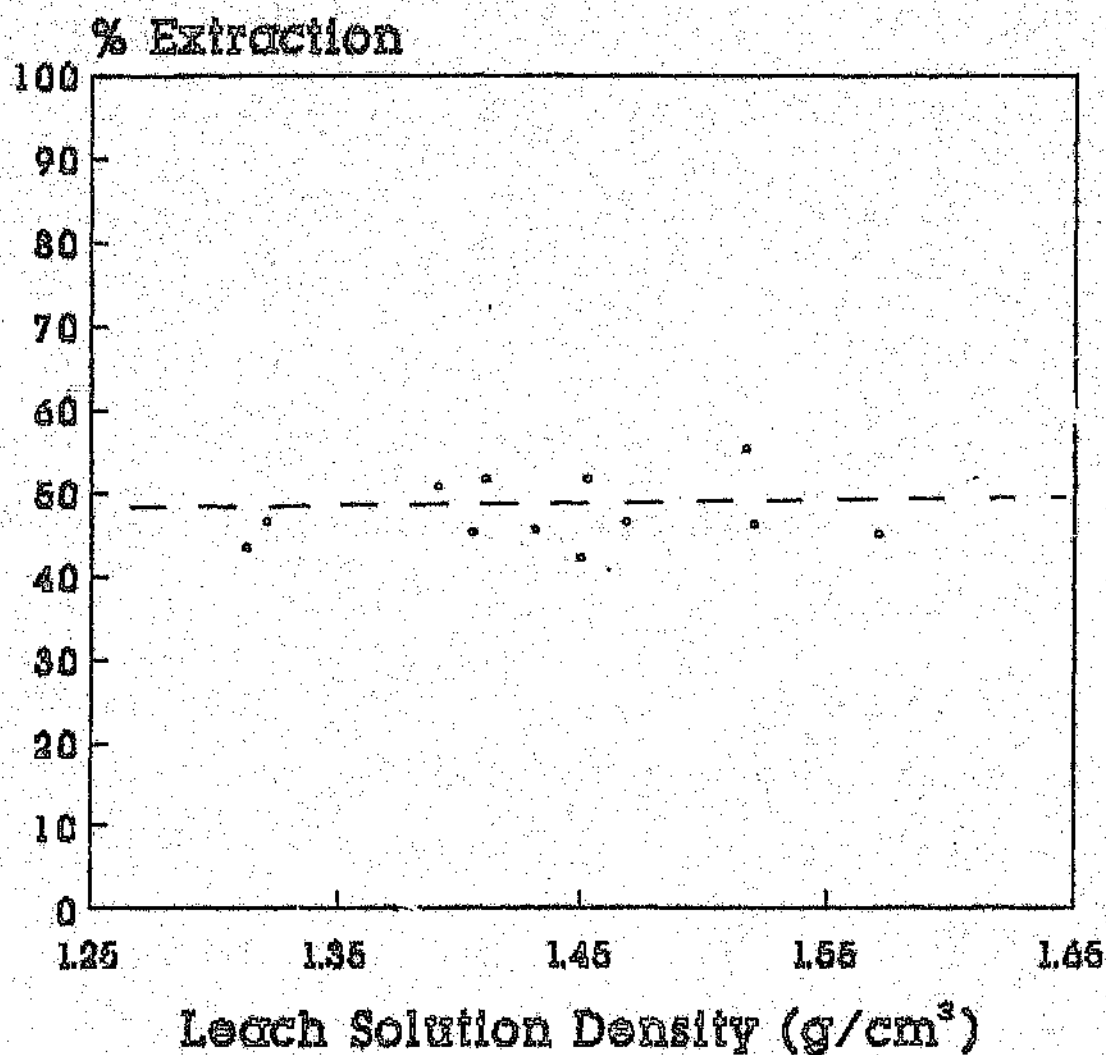
• Rhodium (Rh)

Figure 16
Density Vs % Extraction
Roasted Concentrate



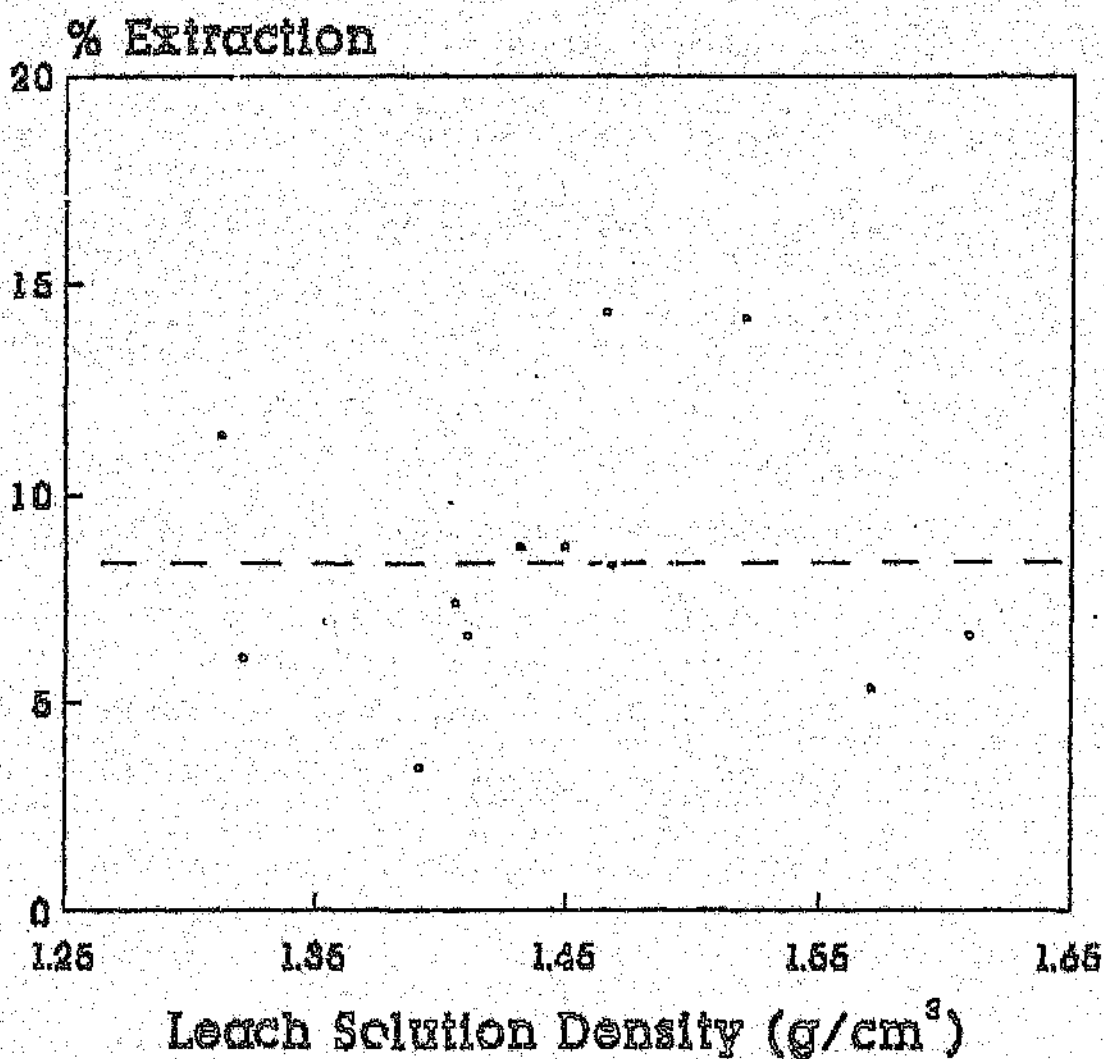
Nickel (Ni)

Figure 17
Density Vs % Extraction
Roasted Concentrate



• Iron (Fe)

Figure 18
Density Vs % Extraction
Roasted Concentrate



• Chromium.(Cr)

The results of leaching when using different concentrations of zinc chloride both for the direct and the roasted concentrates indicated similar extractions, particularly for platinum, palladium and rhodium. The only difference between the two sets of results, Table 6 and 7, is that leaching of the roasted concentrate resulted in the previously established increased platinum group metal extraction.

Since the solubility of the platinum group metals will be governed by the availability of chloride ions, it is the availability of the "free", unassociated chloride ions which will be the controlling factor in the platinum group metal dissolution.

Zinc (II) ions are strongly complexed in chloride solution. The type of ion species in solution change mainly as a function of the chloride ion concentration. The following equation (32) represents the various species which can be present in solution :



For low chloride concentration, the main species in solution are Zn^{2+} and ZnCl^+ . For high chloride concentration, the main species in solution are ZnCl_3^- and ZnCl_4^{2-} .

Thus accordingly the following situation arose in the leaching solutions :

At a relatively low concentration of Cl^- (4.452M), zinc chloride concentration of 2.226M (Density 1.31g/cm³), the dominant zinc species in solution would be ZnCl^+ . Hence the total amount of free chloride ions would be from the dissociated zinc chloride as well as those from the hydrochloric acid and be in the order of 3.32M.

At a relatively high concentration of Cl^- (11.13M), zinc chloride concentration of 5.565M (Density 1.64g/cm³), the dominant zinc species in solution would be ZnCl_3^- and ZnCl_4^{2-} . However, the zinc species in solution would be in an active equilibrium with one another as represented in the equation (32) above due to the high Cl^- concentration. If it is postulated that at any given time, under this high chloride ion concentration approximately 70% of the zinc species were in the ZnCl_3^- and ZnCl_4^{2-} forms, then the total amount of free Cl^- ions would be in the order of 3.66M.

At a middle order concentration of Cl⁻ (7M), zinc chloride concentration 3.5M (Density 1.44g/cm³), the zinc species in solution can be represented equally by the equation (32) with no single dominating species. Thus at any given time, approximately 60% of the total chloride ions present would be associated with zinc metal ions. Hence the total concentration of free chloride ions would be in the order of 3.24M.

It can be concluded that under the leaching conditions of relatively low (2.226M), medium (3.5M) and high (5.565M) zinc chloride concentrations, the availability of free unassociated chloride ions within the leach solution were approximately equal.

That is, the available chloride ion concentration for the dissolution of the platinum group metals were in the range of 3.24 to 3.46M. Thus resulting in the similar extractions of platinum, palladium and rhodium which were experienced when different concentrations of zinc chloride were used in the leach reagent.

That is, the use of different concentrations of zinc chloride resulted in similar amounts of free chloride ions being present in the leaching solution and thus resulted in similar, comparable degrees of platinum group metal extractions between the different zinc chloride concentrations.

For direct leaching, the apparent dependency shown by the degrees of extractions towards concentrations of zinc chloride was a secondary effect. The primary effect was the temperature dependency of the rate of extraction of the platinum group metals. At higher zinc chloride concentration, leaching temperature was higher, thus the degree of extraction from the unroasted concentrate increased. (Leaching was always carried out in the boiling state of the leach reagent) It was this effect of the temperature which provided for the increase in the extraction of platinum group metals.

It is concluded that within this zinc chloride concentration range (2-6M), the chloride ion concentration which was needed for the dissolution of the platinum group metals through the formation of the soluble chlorocomplexes, was not a controlling or limiting factor in the extraction of the platinum group metals from the roasted concentrate. However, the concentration did play a role when direct leaching of the concentrate was done due to its influence on the leaching temperature.

This implies that, the main controlling factor concerned with the dissolution will be the accessibility of the leach reagent towards the platinum group metals.

This is evident owing to the fact that extraction of the platinum group metals from the roasted concentrate was higher than that found in the direct leaching. That is, roasting of the concentrate prior to the oxidative chloride leach increased the accessibility of the leach reagent to the platinum group metals. Thus resulting in higher degrees of extractions.

3. Oxidant Concentration

a. Leaching Of Roasted Concentrate

When the oxidant, nitric acid, concentration was varied from 5.48% to 24.97%(wt/vol), it resulted in a similar degree of extraction for the platinum group metals of platinum, palladium and rhodium.
(Table 8, Figure 19)

Table 8 : Oxidant Concentration vs % Extraction.

[HNO ₃] %(wt/vol)	Percentage Extraction		
	Pt	Pd	Rh
5.48	92.0	72.4	81.2
10.04	93.4	75.0	82.9
11.24	89.4	77.6	75.5
18.73	88.7	76.9	77.4
24.97	92.8	80.1	83.0

Note: All leaching were carried out under similar conditions, using roasted concentrate.
Roasting done at 450°C for 1 hr.

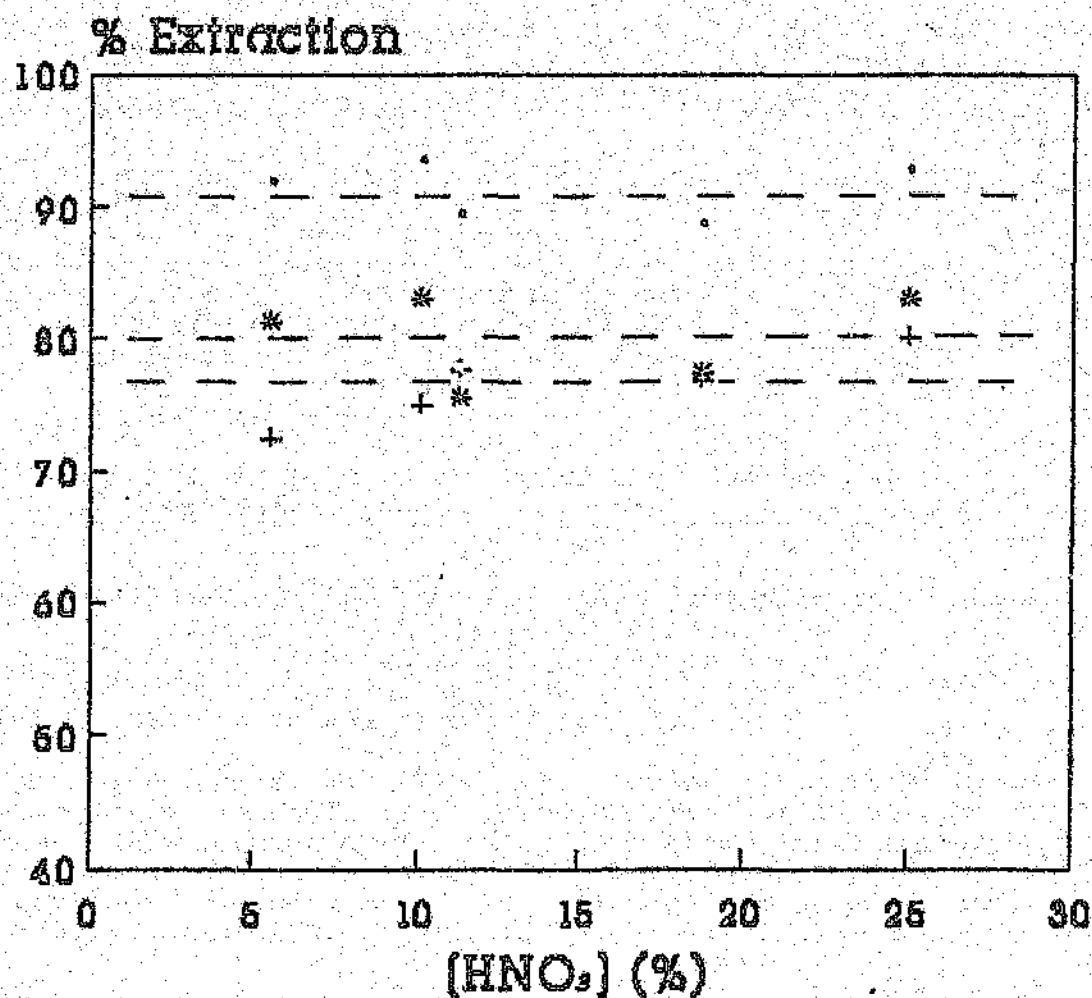
This apparent independence of the degree of extraction towards the oxidant concentration can be explained by the fact that the leaching time was relatively short, only 2.5 to 3 hours. This short time resulted in preventing the large loss of nitric acid through its decomposition. It can be concluded that, the extraction of platinum group metals when utilizing the leaching reagent, zinc chloride/hydrochloric acid/nitric acid occurred at a extremely rapid rate.

Thus when the level of nitric acid, which was continuously reduced through decomposition, reached the stage when it would prevent further dissolution of the platinum group metals, the dissolution had already been completed.

This affect of the oxidant concentration being a non-limiting factor within the above concentration range, was highlighted when the oxidant was added incrementally during the leach.

When the nitric acid concentration was kept constant throughout the leaching process it was established that the extraction of the platinum group metals were comparable to those in which all the oxidant was added initially.

Figure 19
Oxidant Concentration Vs % Extraction
Roasted Concentrate



• Platinum (Pt) + Palladium (Pd)
* Rhodium (Rh)

3. Oxidant Concentration

b. Direct Leaching Of Concentrate

The direct leaching of the concentrate showed a similar trend of the non-dependence of the platinum group metal extraction towards the oxidant, nitric acid, concentration.

(Table 9, Figure 20)

Table 9 : Oxidant Concentration vs % Extraction.

[HNO ₃] % (wt/vol)	Percentage Extraction		
	Pt	Pd	Rh
10.12	80.7	81.2	65.7
10.21	80.0	79.9	63.5
12.48	77.0	81.2	61.6
20.81	78.6	84.2	63.3

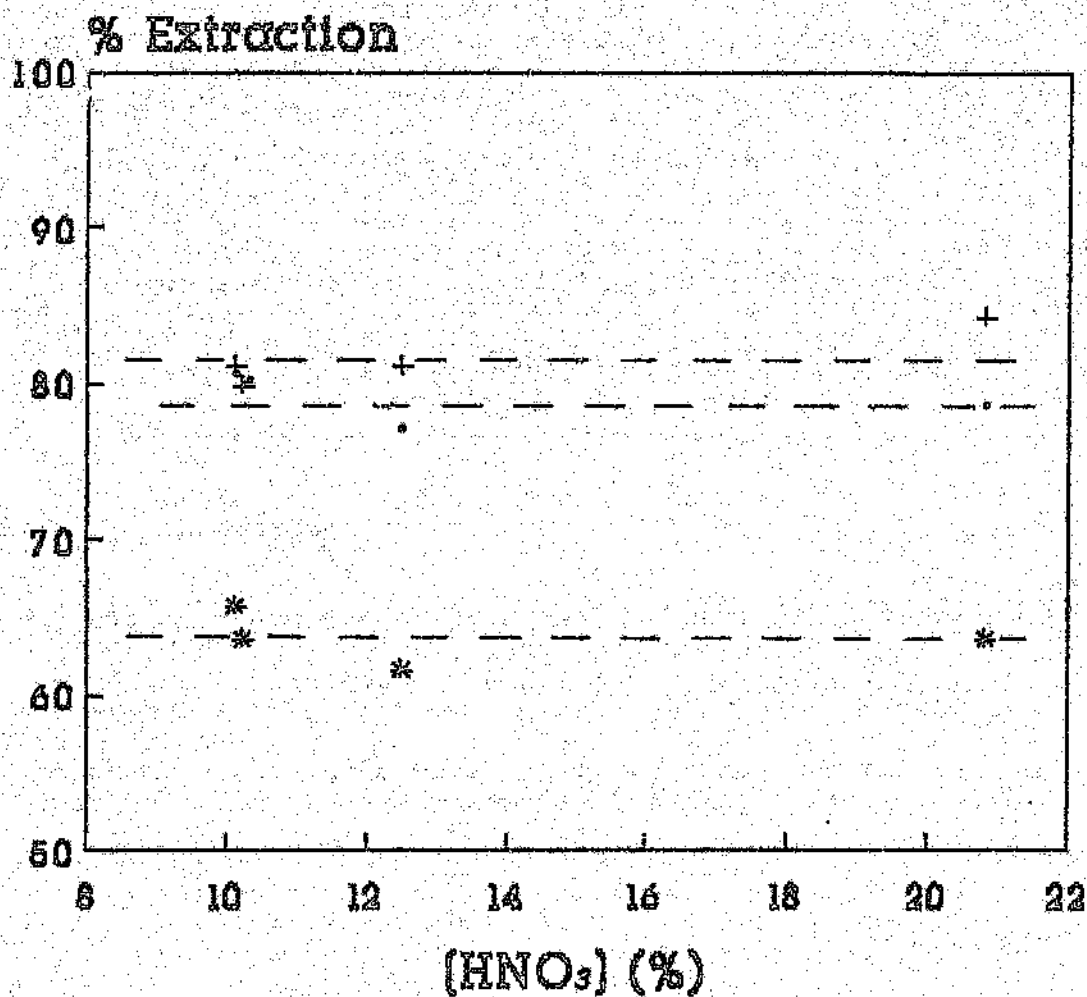
Note: All leaching were carried out under similar conditions.

One can conclude from the results of leaching the roasted and non-roasted concentrate, that the apparent independence of the extraction on the oxidant concentration indicates that the dissolution of the platinum group metals occurred rapidly.

It must be noted that a large proportion of the nitric acid (oxidant) would be used in the dissolution of other non-platinum group metals as well as being lost through its decomposition which was clearly visible during the leachings by observing the evolution of red-brown gaseous products. (NO_x - type gaseous products)

The use of the zinc chloride/hydrochloric acid mixture as the source of the chloride ions resulted in the high activity of the chloride ions towards platinum group metals complexation. Hence, provided that there was an adequate amount of oxidant present, the dissolution of platinum group metals by chloro-complexation occurred readily and rapidly.

Figure 20
Oxidant Concentration Vs % Extraction
Direct



• Platinum (Pt)
* Rhodium (Rh)

+ Palladium (Pd)

4. Leaching Temperature

a. Direct Leaching Of Concentrate

The liberation of platinum group metals from refractory minerals, particularly the kinetics of platinum group metal sulphide and arsenide oxidation, are highly dependent on the leaching temperature. This effect was highlighted when direct leachings of the concentrate were carried out.
(Table 10, Figures 21 & 22)

Table 10 : Leaching Temperature vs % Extraction.

Temperature (°C)	Percentage Extraction					
	Pt	Pd	Rh	Fe	Ni	Cr
84-87	66.4	68.2	59.7	57.5	91.9	16.3
103	74.6	80.1	59.4	59.6	93.4	14.1
108	80.7	81.2	65.7	60.4	89.2	14.2

Note : Leaching were carried out under similar conditions.

Both platinum and palladium showed a substantial increase in their degrees of extractions when the leaching temperature was increased. Rhodium extraction also increased with higher temperatures, however the effect was less marked.

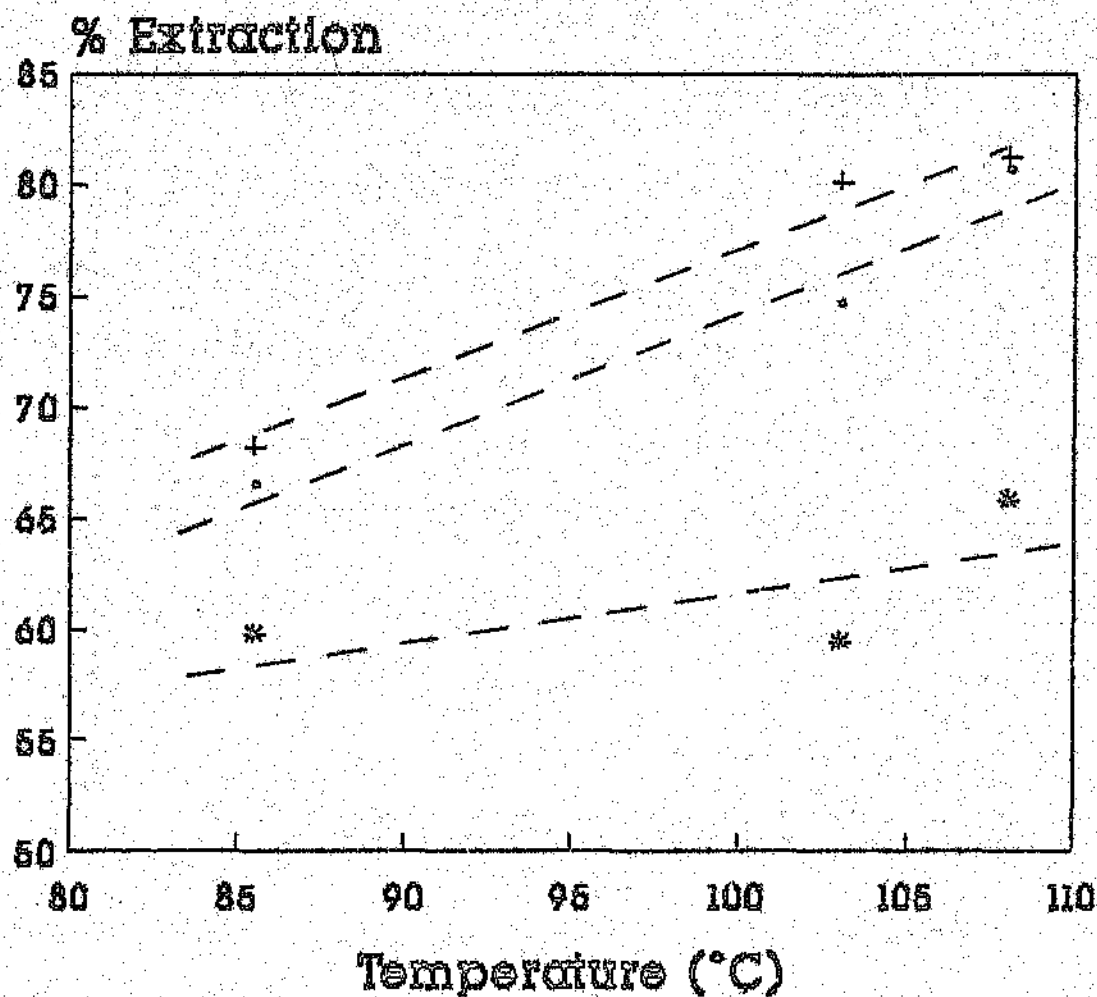
Extraction of the base metals, nickel, iron and chromium showed no real dependency towards leaching temperature.

There exists an upper temperature limit for the leaching due to the stability of the leach reagent.

The pyrohydrolysis reaction of zinc chloride will result in the loss of stability of the leach reagent, however this only occurs at temperatures of greater than 124°C.

This loss of stability of the leach reagent would not have been a factor in the leaching experiments, since the leaching temperature was always below 124°C.

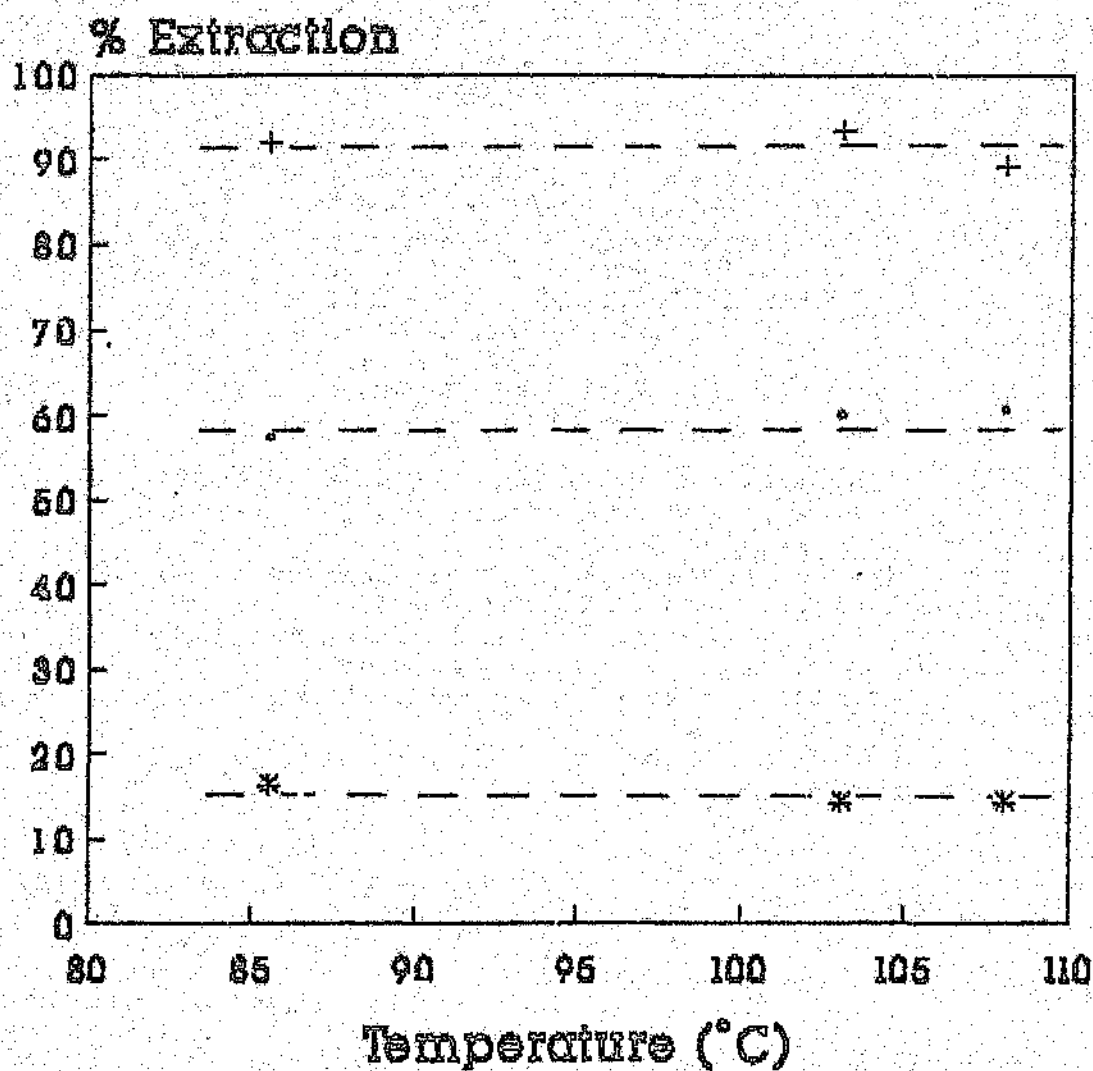
Figure 21
Leach Temperature Vs % Extraction
Direct



• Platinum (Pt)
* Rhodium (Rh)

+ Palladium (Pd)

Figure 22
Leach Temperature Vs % Extraction
Direct



• Iron (Fe) + Nickel (Ni) * Chromium (Cr)

4. Leaching Temperature

b. Leaching Of Roasted Concentrate

When roasted concentrate was used and the leach temperature was varied, there was no definite increases in the degree of extraction of platinum, palladium or rhodium.

(Table 11, Figures 23 & 24)

Table 11 : Leaching Temperature vs % Extraction.

Temperature (°C)	Percentage Extraction					
	Pt	Pd	Rh	Fe	Ni	Cr
105	193.4	175.0	182.9	146.1	189.2	8.3
110	189.4	177.6	175.5	141.9	185.7	8.7
110	195.4	180.2	186.5	150.5	192.5	3.4
114	188.7	176.9	177.4	151.2	192.5	6.6
123	192.0	172.5	181.2	129.9	176.5	1.7

Note : Leaching were carried out under similar conditions. Concentrate roasted at 650°C for 1hr.

This was expected since during the pretreatment of the concentrate, the roasting procedure, resulted in oxidation of the concentrate minerals.

That is, the sulphide minerals present in the concentrate were oxidized according to the general reaction :



Thus the dependency of the kinetics of platinum group metal sulphide oxidation on the leaching temperature would no longer be an influencing factor. Hence, the extractions of platinum, palladium and rhodium from the roasted concentrate would not be affected to any large degree by the leaching temperature.

Provided that the leach reagent was in its boiling state, extractions were effectively independent of the leach temperature.

Data obtained when plotted for the shrinking core model and diffusion controlled mechanism of leaching did not support either of the two mechanisms. However the data obtained was insufficient to establish any adequate conclusions.

Figure 23
Leach Temperature Vs % Extraction
Roasted

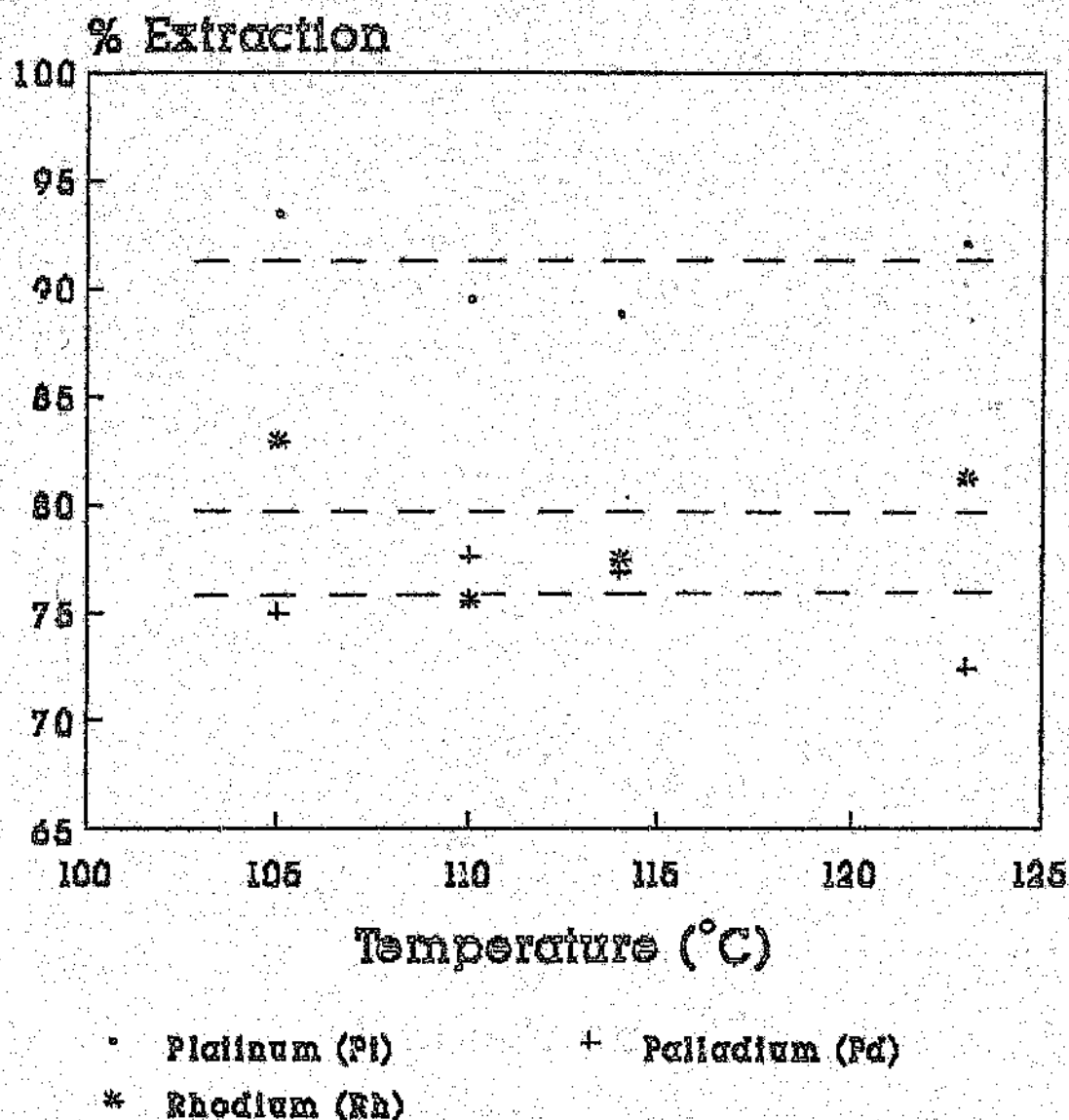
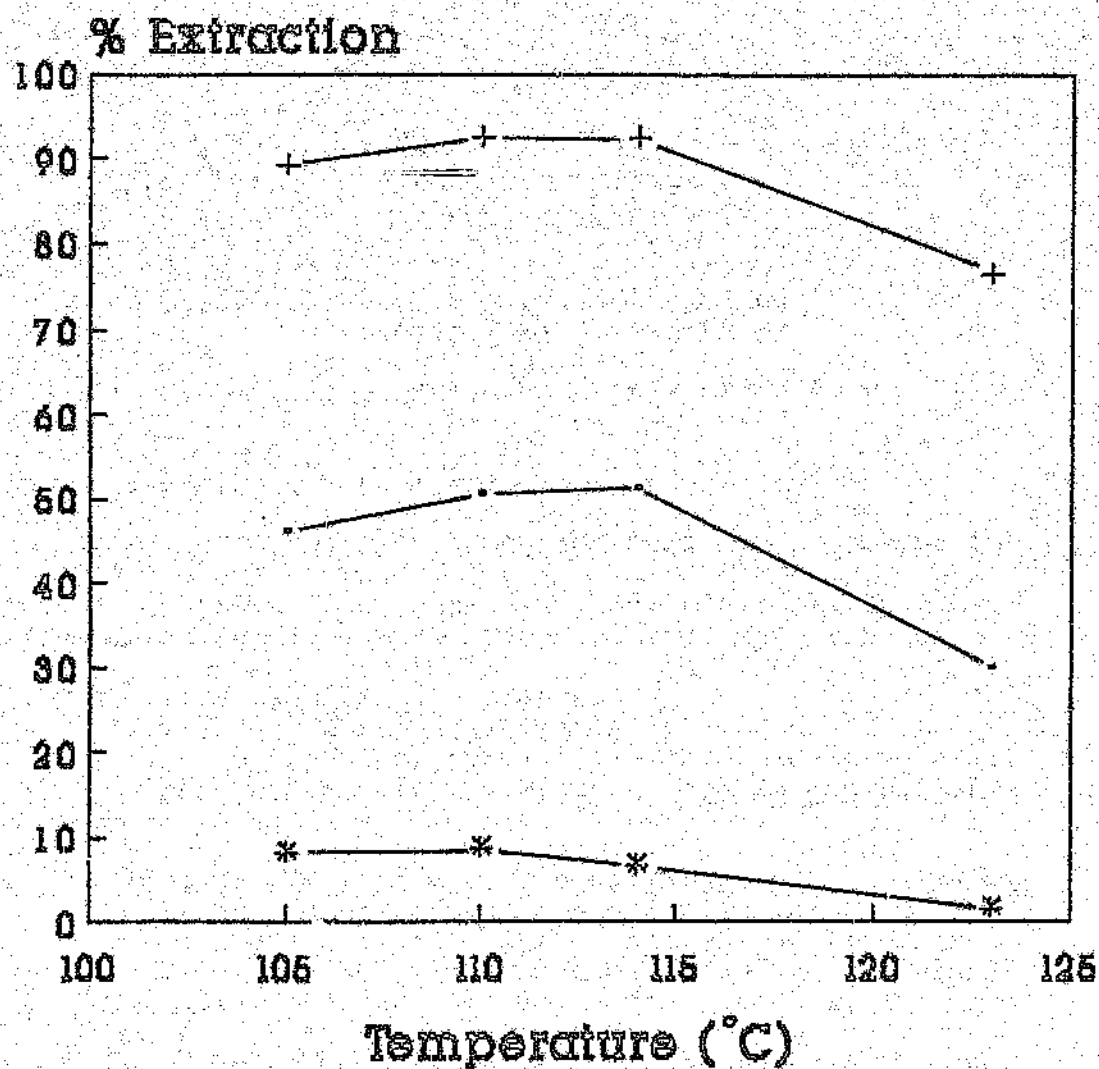


Figure 24
Leach Temperature Vs % Extraction
Roasted



• Iron (Fe) + Nickel (Ni) * Chromium (Cr)

5. Leaching Time

Leaching of the roasted concentrate with only the time of leaching being varied indicated that the extraction of platinum, palladium and rhodium, was extremely rapid and increased to a maximum level after 1.5 hours before showing a gradual decrease. The base metals, iron and nickel also showed this rapid extraction.
(Table 12, Figures 25-28)

Table 12 : Leaching Time vs % Extraction.

Leach Time (Hours)	Percentage Extraction				
	Pt	Pd	Rh	Fe	Ni
0.25	169.3	185.5	170.1	136.4	144.5
0.50	186.3	172.3	181.1	140.0	181.0
1.5	195.4	180.2	186.5	150.5	192.5
2.5	192.0	179.1	183.1	149.1	187.5
3.0	189.1	181.6	176.2	145.1	183.0

Note : Leaching were carried out under similar conditions. Concentrate roasted at 650°C for 1hr.
[ZnCl₂] 3.6729M; HNO₃ 10-12.5%; Temp 105°C-110°C.

This rapid extraction, especially for platinum, palladium and rhodium can be explained by the following factors :

- (i) Pretreatment of concentrate.
Roasting of the concentrate at 650°C for 1 hour prior to leaching, resulted in the oxidation of sulphidic minerals and hence liberated the platinum group metals.
- (ii) Kinetics of platinum group metal sulphide oxidation.
Roasting of the concentrate prior to leaching effectively nullified the relative slow kinetics of platinum group metal oxidation which occurs during the direct leaching of sulphidic minerals.
- (iii) The high concentration of chloride ions in the leach reagent drove the formation of soluble complex chlorides to completion.
That is, the high chloride ion content of the leaching solution caused a rapid dissolution of the liberated platinum group metals via fast formation of the soluble chlorocomplexes.
The platinum group metals being liberated during the roasting procedure.

Tyson and Bautista⁽²⁰⁾ also established that the rate of both platinum and palladium dissolution into a relatively weak Aqua Regia solution was rapid and started at a relatively high value.

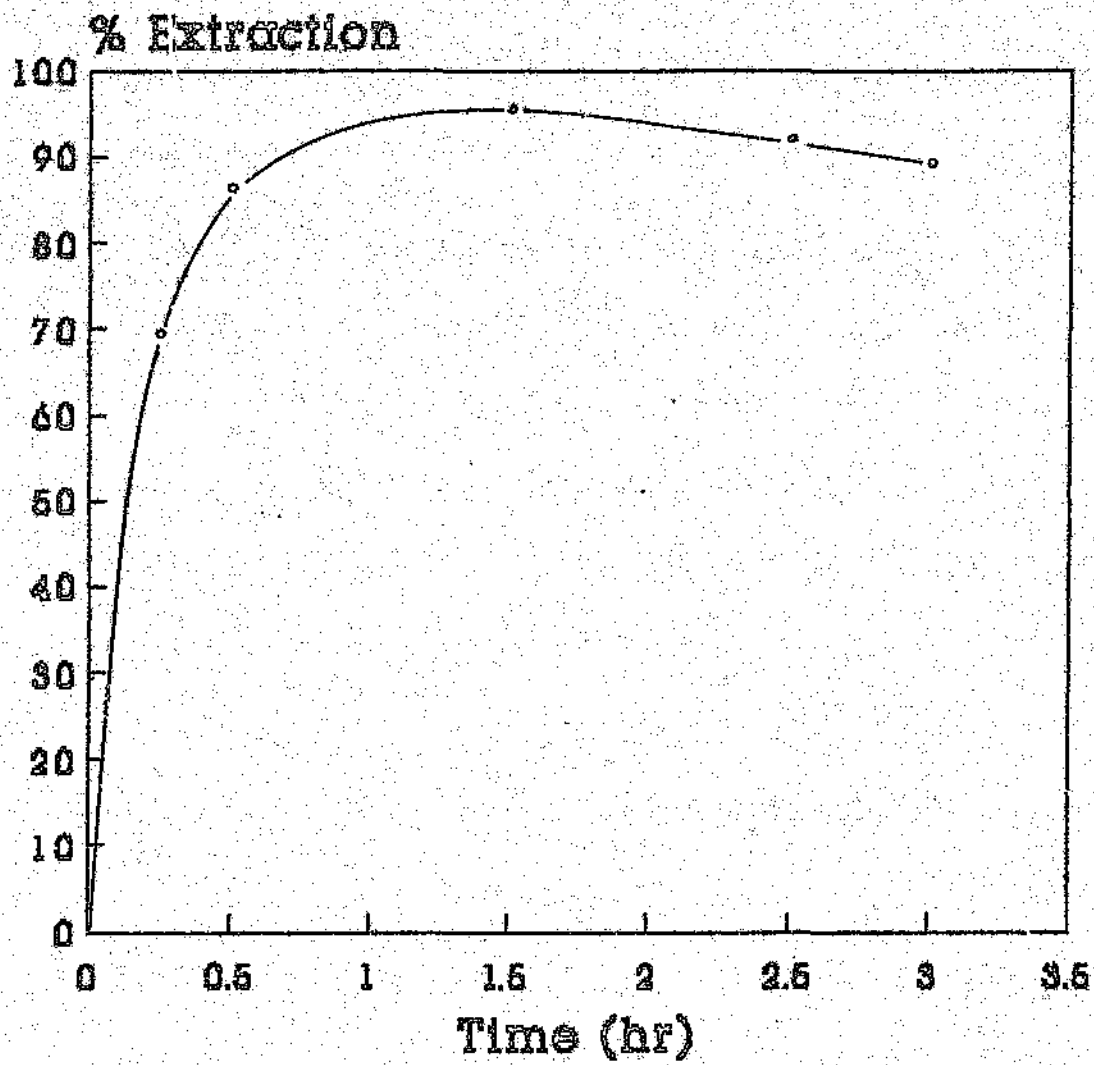
The rapid extraction by the zinc chloride based leach reagent, with the maximum level reached after 1.5 hours also explained why there was no apparent effect of the dissolution rates towards oxidant concentration. Since the dissolution of the platinum group metals were fast, the majority being dissolved after only half an hour, the initial oxidant concentration during this period would always be relatively high. Thus result in a situation in which there was a sufficient concentration of oxidant present and hence in an apparent non-dependency of the oxidant concentration on the degree of platinum group metal extraction.

The decrease in percentage extraction of platinum and rhodium (Figures 25 & 27), as the leach time was extended is a result of the establishment of the complex equilibria involved for the chlorocomplex formation within the leaching solution.

Also the loss of chloride ions from the leach reagent can not be excluded even though the majority of HCl gas produced during the leaching would be returned to the reactor via its dissolution in the condensed water vapor.

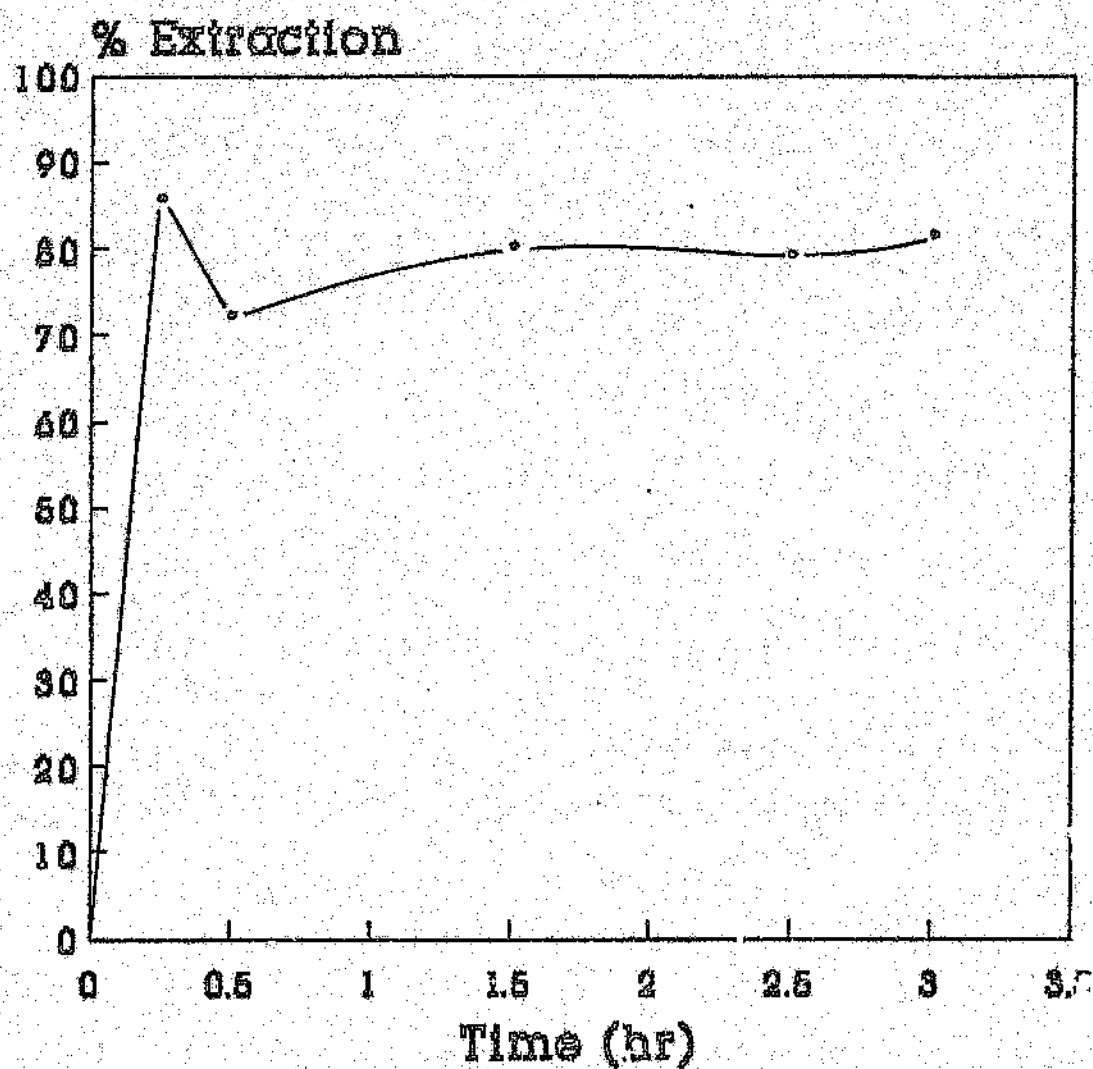
The decrease in the degree of iron extraction as leach time was extended indicates that there was precipitation of iron from solution, most likely as a result of hydrolysis.

Figure 25
Leach Time Vs % Extraction
Roasted



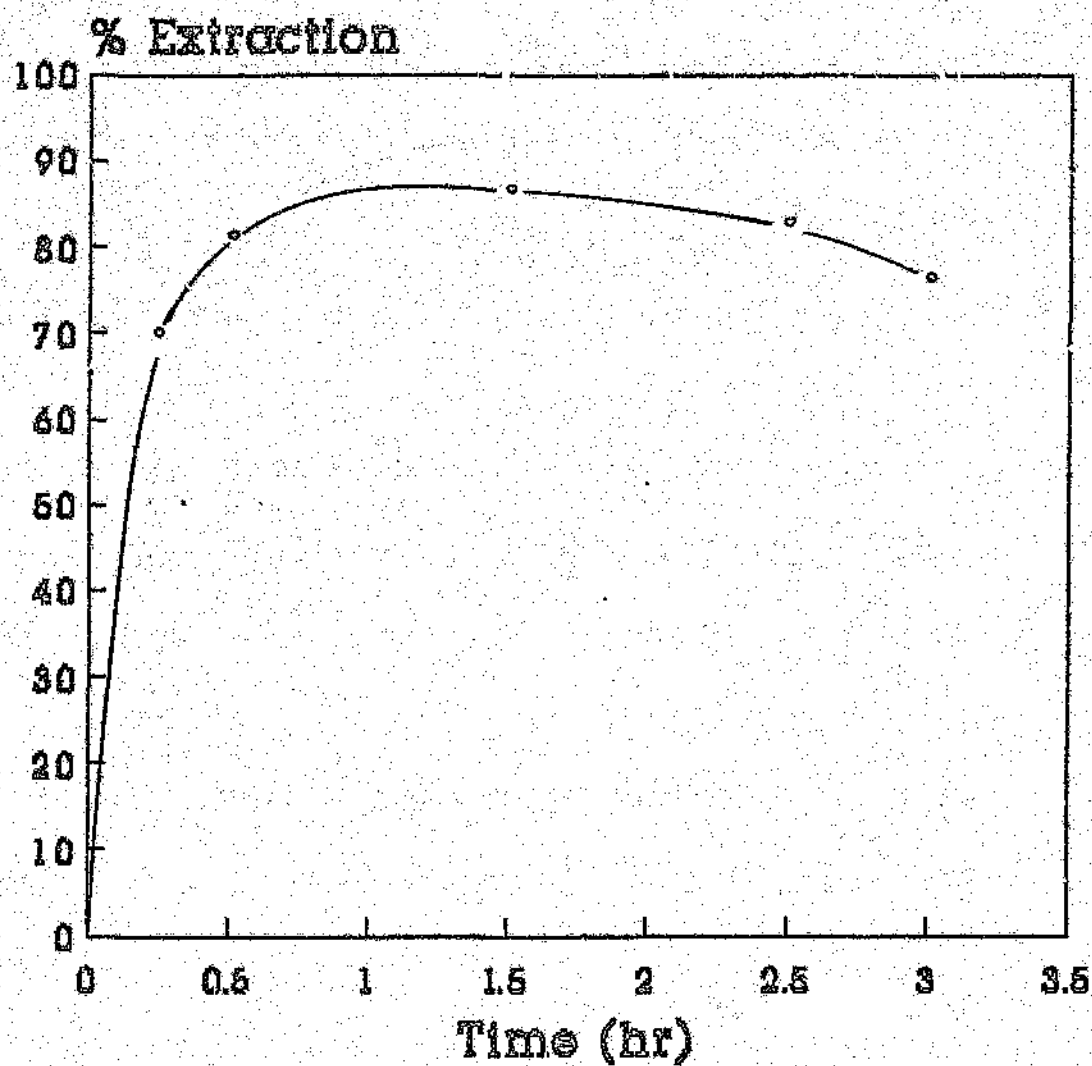
* Platinum (Pt)

Figure 26
Leach Time Vs % Extraction
Roasted



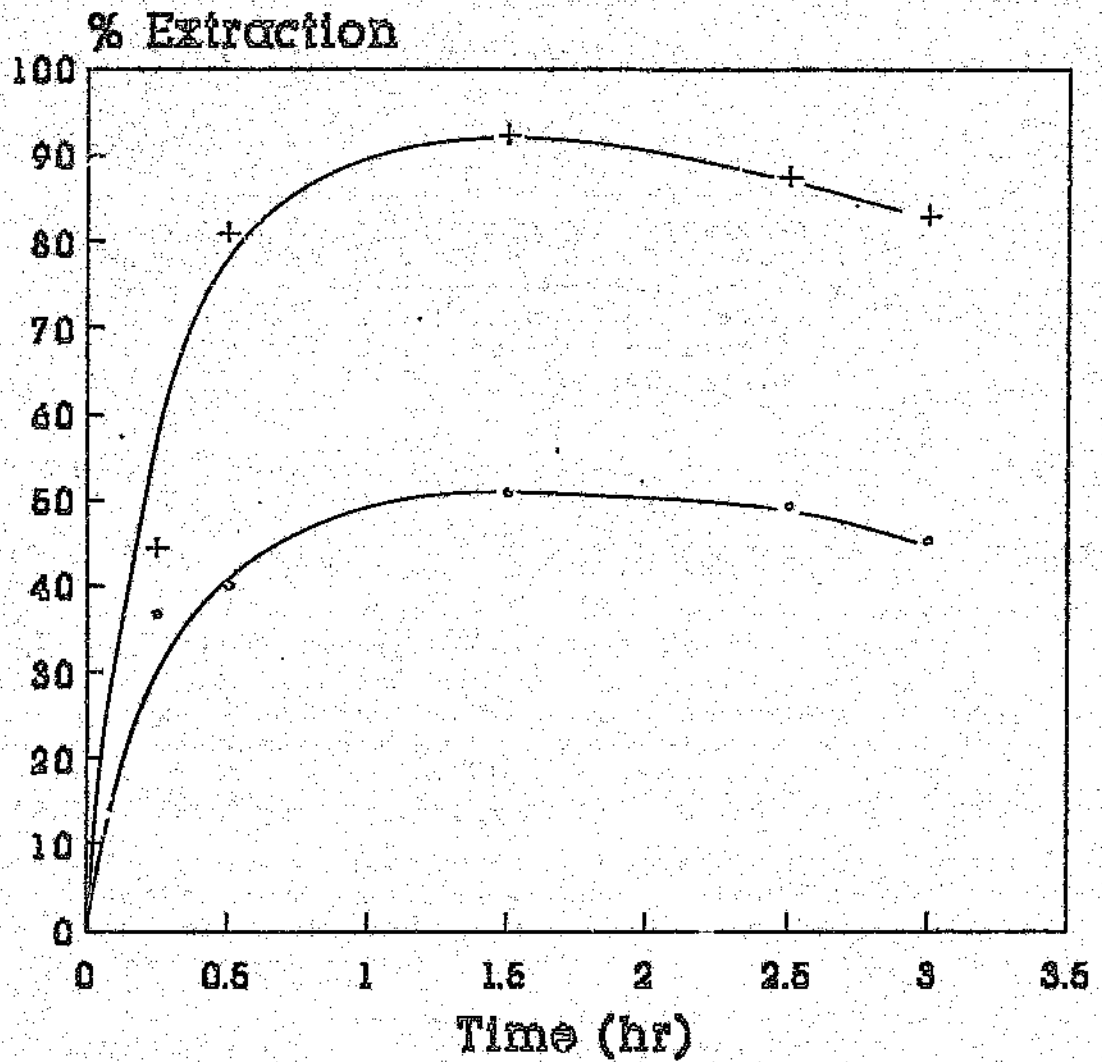
• Palladium (Pd)

Figure 27
Leach Time Vs % Extraction
Roasted



• Rhodium (Rh)

Figure 28
Leach Time Vs % Extraction
Roasted



° Iron (Fe) + Nickel (Ni)

6. Three Stage Leaching

A three stage leaching, as shown in Figure 29, was carried out using the roasted concentrate. At each leaching stage a new, "fresh" leach solution ($\text{ZnCl}_2/\text{HCl}/\text{HNO}_3$) was used in order to obtain maximum extractions, particularly for platinum, palladium and rhodium.

The following results were obtained :
(Table 13, Figures 30,31)

Table 13 : Three Stage Leaching.

Leach Stage	Leach Time ¹	Percentage Extraction ²					
		Pt	Pd	Rh	Fe	Ni	Cr
1	3	193.4	175.0	182.9	146.1	189.2	8.2
2	6	196.4	193.2	187.7	161.1	194.8	8.4
3	9	198.4	193.2	191.6	166.2	196.6	12.9

Note : 1 - Cumulative Leach Time.

2 - Cumulative Percentage Extraction.

All leaching were carried out under similar conditions.

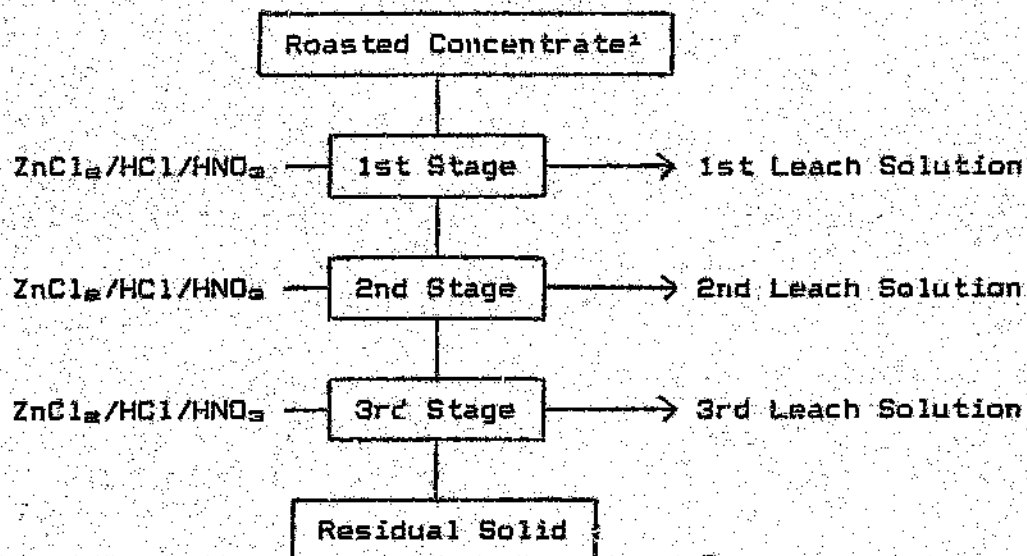
The use of "fresh" solution for the leaching of the residual solid resulted in a high overall extraction of the platinum group metals. All three, platinum, palladium and rhodium were extracted to levels of greater than 90%. Platinum 98.4%, Palladium 97.3% , Rhodium 91.6% after leaching for 9 hours.

The use of "fresh" leach reagents insured that there would be a high concentration of available chloride ions and oxidant present during leaching. Thus allowing for maximum platinum group metal dissolution.

For rhodium extraction, the increase in the degree of extraction can be attributed to the relatively slow kinetics involved in the formation of the chlorocomplex, RhCl_4^{3-} (7), as well as, to the tendency of the metal to form a kinetically inert layer of chloride (or oxide) at its surface.

Thus a longer leach time was required for the dissolution of rhodium in order to obtain a degree of extraction which was comparable to that of platinum and palladium.

Figure 29 : Three Stage Leaching



Note 1 : Roasting at 650°C for 1 hour

Figure 30
Solid Residue Leaching
PGM Extraction

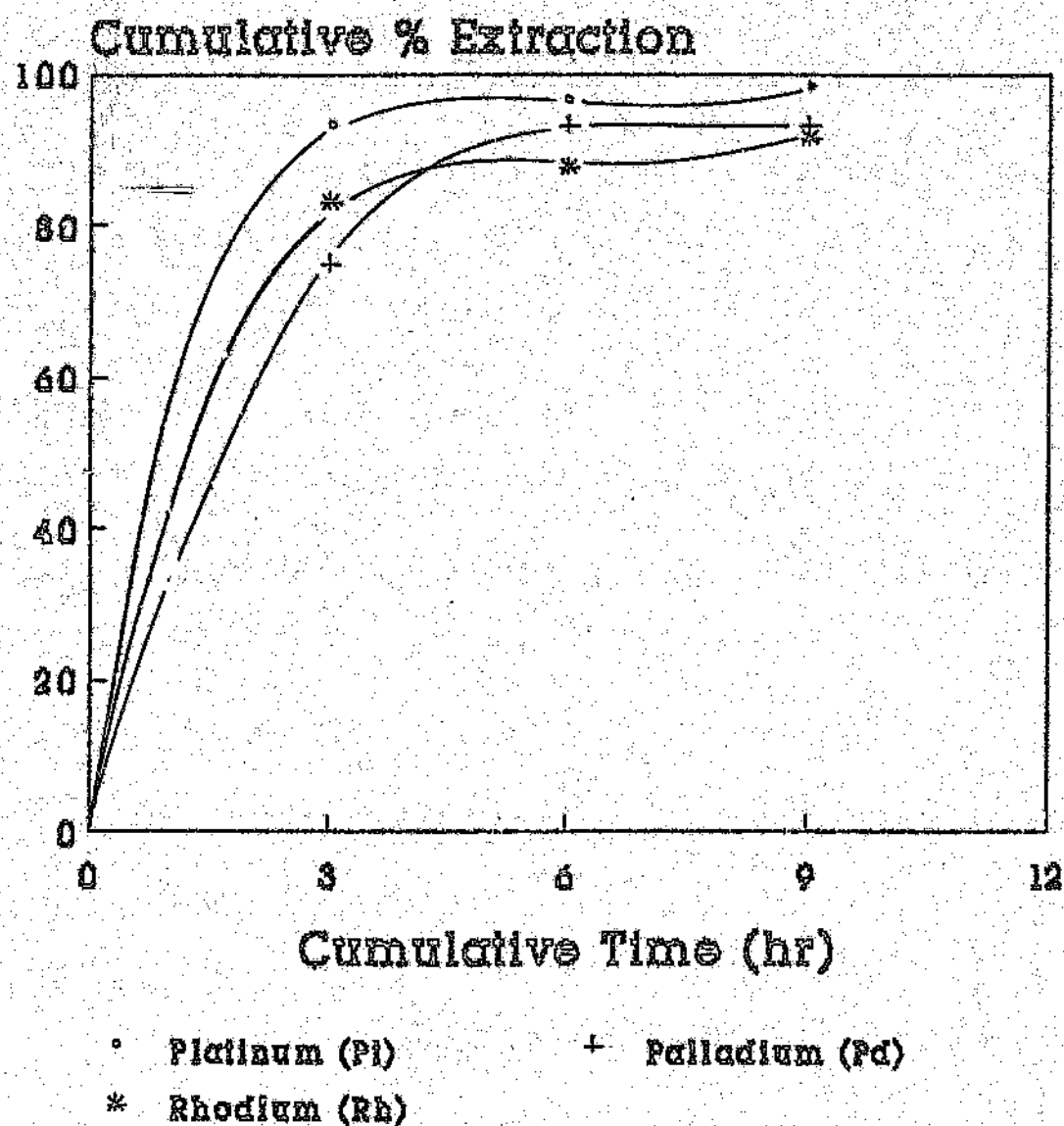
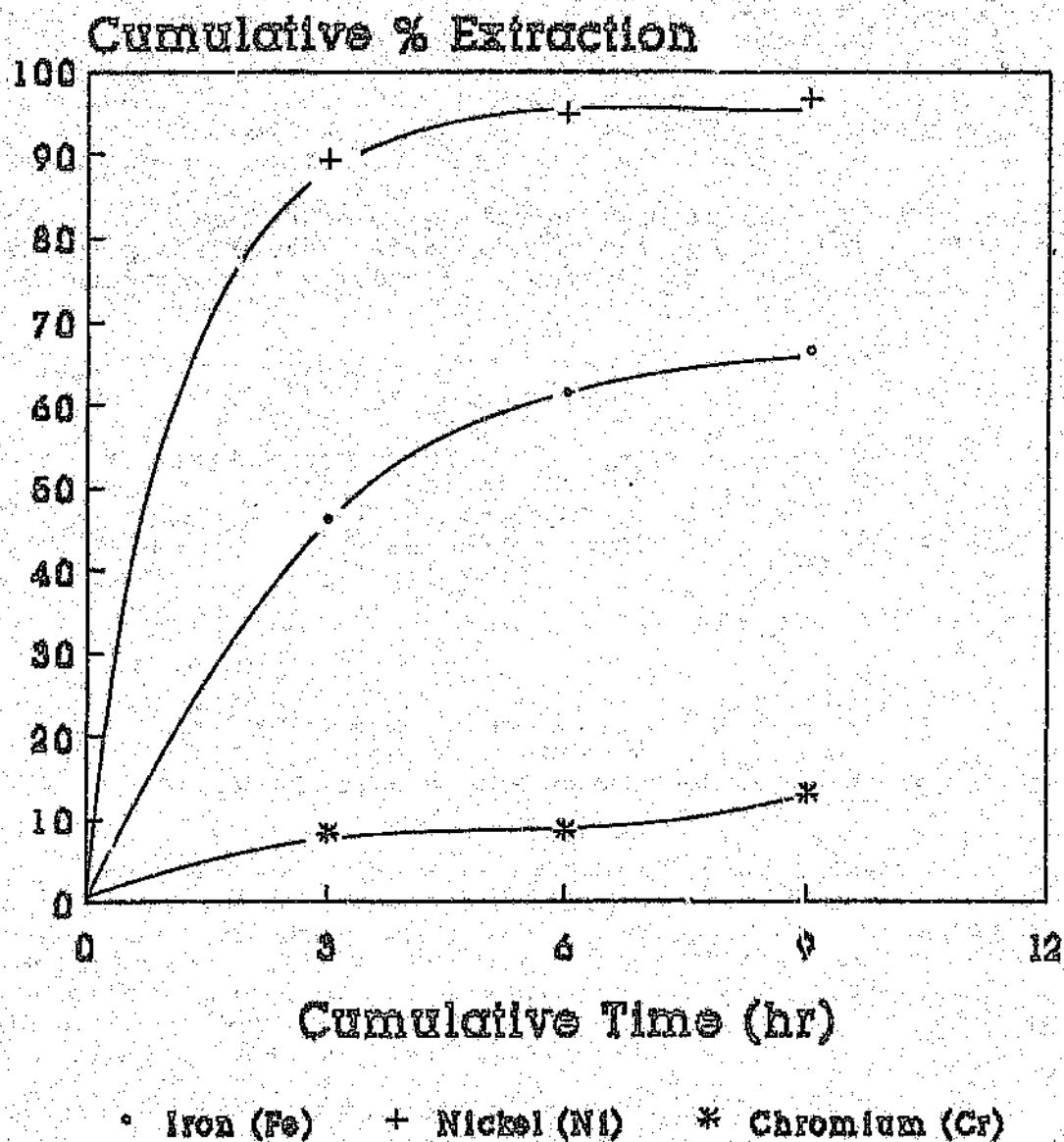


Figure 31
Solid Residue Leaching
Base Metal Extraction



Amongst the other metals considered, only nickel was extracted to a level of greater than 90%. However, of the three base metals, it was iron which showed the greatest increase in extraction from 1st to 3rd leaching stage, increasing from 46.1% to 66.2%.

This increase in iron dissolution as the overall time of leaching was extended, strongly supports the view that the iron oxide, Fe_2O_3 , was formed during the roasting procedure.

Even though the iron oxide, Fe_2O_3 , is essentially alkaline, it reacts slowly with acids.⁽²²⁾ Hence the need for a longer reaction time for its dissolution.

It is interesting to note that during each subsequent leaching stage, the percentage weight loss of the solid decreased markedly from one stage to the other.

Table 14 : Residual Solid Leaching
Percentage Weight Loss.

Leach Stage	Leach Time ¹	Weight Loss Percentage ²
1	3	15.62
2	6	7.33
3	9	2.29

Note : 1 - Cumulative Leach Time.

2 - Percentage Weight Loss During Leach.

All leach carried out under similar conditions.

This indicated that there was a fairly substantial proportion of the concentrate that was insoluble under these leaching conditions. This can be related to a large amount of unreactable silicate present within the concentrate, together with a portion of non-soluble metal oxides which were formed during the pretreatment of the concentrate. That is, the roasting stage.

However, even so the excellent extraction of platinum, palladium and rhodium indicated that there was no detrimental effect caused by the roasting of the concentrate. In fact, as stated previously the pretreatment of the concentrate had a definite advantage toward improving the extractions of the platinum group metals.

7. Distribution Of Extracted Metals

A typical distribution of the extracted metals within the leach and wash solutions after leaching of the concentrate and washing of the residual solid material are shown below.

Table 15 : Extracted Metal Distribution.

Solution	Percentage Distribution ¹					
	Pt	Pd	Rh	Fe	Ni	Cr
Leach Reagent	89.75	89.31	89.21	89.53	89.49	88.71
Acid Wash	9.58	9.88	9.86	9.75	9.88	10.56
Water Wash 1	0.51	0.62	0.59	0.53	0.48	0.45
Water Wash 2	0.16	0.19	0.34	0.19	0.15	0.28

Note : 1 - Percentage distribution of amounts of extracted metals.

Acid Wash was a solution of 1:1 HCl:H₂O.

It is evident that approximately 90% of the extracted metals, both the platinum group and base metals, were found in the zinc chloride/hydrochloric acid/nitric acid leach solution.

This was expected since the high chloride ion content of the leach reagent provided for the dissolution and maintained solubilization of the metals, especially true for the platinum group metals. The high chloride content ensured that the platinum group metals were maintained in their soluble chlorocomplex configuration in the leaching reagent.

The acid wash, a 1:1 ratio HCl to H₂O, contained approximately 9% of the platinum group metals. This acid wash ensured that if any loss of the platinum group metals occurred by precipitation, they would be redissolved due to the application of a solution containing free chloride ions.

The water washes contained less than 1% of the total extracted metals.

For the base metals, nickel, iron and chromium, an almost identical distribution pattern was found. Again explained by the availability of chloride ions in order for soluble complex formation.

The distribution of the dissolved metals being associated to the amount of chloride ions present thereby allowing for chlorocomplex formation.

This system of washing of the residual solid, first with an acid wash followed by water washing had the added benefit of enabling maximum extractions of the metals from the concentrate.

Thus, the residual solid that was to be discarded was essentially stripped of all of the valuable materials present in the initial concentrate.

The washing procedure also ensures for environmental protection on the disposal of the solid residual.

This type of distribution of the extracted platinum, palladium, rhodium, iron, nickel and chromium has the added advantage when considering their recovery. Since the majority of the dissolved/extracted metals, particularly the platinum group metals, occur in one solution, that is the leach solution, techniques for the recovery of the metals possibly need only to concern one type of solution.

A PGM recovery process based on the utilization of only one type of solution, the leaching solution, will definitely be much more cost effective than one which concerns the use of a number of different types of solutions.

Summary Of Conclusions

1. Clearly the use of the zinc chloride based leaching reagent was not detrimental to the extraction of the platinum group metals, platinum, palladium and rhodium when compared to that of Aqua Regia leaching. The use of the metal chloride based leach reagent resulted in a higher leaching temperature, hence levels of extractions of platinum, palladium and rhodium were comparable with one another.

Average degree of extraction for the metal chloride based leach reagent were :

Leach	Platinum	Palladium	Rhodium
Direct	78.64%	81.03%	64.50%
Roasted	90.85%	79.46%	80.12%

The use of zinc chloride/hydrochloric acid mixture as the source of chloride ions resulted in a high activity of chloride ions towards platinum group metal complexation.

Provided there was an adequate amount of oxidant present, dissolution of platinum, palladium and rhodium occurred readily and rapidly.

2. Within the zinc chloride concentration range of 2M to 6M, the chloride ion concentration which was required for the dissolution of the platinum group metals through the formation of the soluble chlorocomplexes, was not a limiting factor in the extraction of the platinum, palladium and rhodium.
3. Roasting of concentrate prior to oxidative chloride leach was beneficial for the extraction of platinum group metals, especially platinum. Since ;
 - i) Roasting resulted in removal of sulphide thereby creating a more readily accessible platinum complex. That is, possible formation of PtO , which dissociated to the metal at temperatures greater than $200^{\circ}C$. and/or
 - ii) The concentrate was a sulphidic mineral concentrate thus roasting caused formation of metal oxides and corresponding SO_2 release which lead to the opening of the mineral structure for greater penetration of the leach reagent.

4. The loss of weight as roasting temperature increased was attributed to an increased loss of sulphide through SO_2 formation.
5. A decrease in the percentage weight loss during the subsequent leaching of roasted concentrate was due to the formation of insoluble material during the roasting procedure.
6. There was rapid extractions of platinum, palladium and rhodium.
Pt 95.4%, Pd 80.2%, Rh 84.5% in 1.5 hours.

Owing to the fact that :

- i) Roasting of the concentrate prior to leaching liberated the platinum group metals by oxidation.
 - ii) The relatively slow kinetics of platinum group metal oxidation which occur during the leaching of a sulphidic concentrate were nullified by the roasting procedure.
 - iii) High concentration of the chloride ions in the leach solution drove the formation of the chlorocomplexes of platinum, palladium and rhodium.
7. The main limiting factor for the dissolution of the platinum group metals was found to be the accessibility of the leach reagent towards platinum, palladium and rhodium.
 8. An oxidant concentration range of 5.48% to 24.97% resulted in similar degrees of extractions. That is, it was not a limiting factor in the extractions of platinum, palladium and rhodium from the concentrate.
 9. For the direct leaching of the concentrate, the degrees of extractions greatly increased when the leaching temperature was increased.

Particularly for platinum and palladium.

Pt increased from 66.4% to 80.7%

Pd increased from 68.2% to 81.2%

For a leach temperature increase from 87°C to 108°C.

10. For the roasted concentrate, the degree of extraction was independent of the leach temperature. This was due to the fact that roasting of the concentrate lead to oxidation of the minerals. Hence the dependency of the kinetics of platinum group metal sulphide oxidation on leach temperature no longer applied.

Pt 93.4% Pd 75.0% Rh 82.9% for leach temperature 105°C
Pt 92.0% Pd 72.5% Rh 81.2% for leach temperature 123°C

11. A three stage leaching of the roasted concentrate lead to high overall extractions of platinum, palladium and rhodium.
Pt 98.4% ; Pd 93.2% ; Rh 91.6%

The use of "fresh" leach reagent insured that there was a high concentration of "free" chloride ions. The the high chloride ion concentration drove the formation of the soluble chlorocomplexes of the platinum group metals.

For rhodium extraction, the increase in the percentage extraction as the leach time increased was attributed to the relatively slow kinetics involved in the formation of the chlorocomplex.

12. High chloride ion concentration of the leach reagent resulted in the majority of the platinum group metals, approximately 90%, being present in the leach solution. Thus resulting in the advantage of only having one type of solution when dealing with the recover of the platinum group metals.

13. The use of metal chloride salts other than zinc chloride as the chloride ion carrier in the leach reagent are possible. Provided that the metal chloride salt has a relatively high solubility which will result in a leach reagent which has a chloride ion concentration in the range of 4 M to 12 M, and it will be stable under the leaching conditions of 105°C to 120°C.

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