

# A Study of the Variables in the Optimisation of a Platinum Precipitation Process

Tebogo Phetla, Edison Muzenda and M Belaid

**Abstract**—This study investigated possible ways to improve the efficiency of the platinum precipitation process using ammonium chloride by reducing the platinum content reporting to the effluent. The ore treated consist of five platinum group metals namely, ruthenium, rhodium, iridium, platinum, palladium and a precious metal gold. Gold, ruthenium, rhodium and iridium were extracted prior the platinum precipitation process. Temperature, reducing agent, flow rate and potential difference were the variables controlled to determine the operation conditions for optimum platinum precipitation efficiency. Hydrogen peroxide was added as the oxidizing agent at the temperature of 85-90°C and potential difference of 700-850mV was the variable used to check the oxidizing state of platinum. The platinum was further purified at temperature between 60-65°C, potential difference above 700 mV, ammonium chloride of 200 l, and at these conditions the platinum content reporting to the effluent was reduced to less than 300ppm, resulting in optimum platinum precipitation efficiency and purity of 99.9%.

**Keywords**—Platinum Group Metals (PGM), Potential difference, Precipitation, Redox reactions.

## I. INTRODUCTION

THIS article concentrates on the processes involved in platinum precipitation using ammonium chloride by reducing the platinum content reporting to the effluent mainly for optimum platinum precipitation efficiency and purity of 99.9%. The main problem encountered during the final precipitation process of platinum was the platinum salt which was not precipitated during the process and as a result the platinum content in the effluent was increased. This has led to poor recoveries and high processing costs, because the effluent has to be further processed to reduce the quantity of platinum in filtrate solution. The problem of platinum not being precipitated in the platinum precipitation process result in the high amount of platinum reporting to the effluent, hence increasing the operation cost due to re-processing of these

material. This problem has led to the investigation on the possible ways to improve the platinum precipitation efficiency to reduce platinum in the effluent.

The world-wide production of the PGMs has increased dramatically over the last century and has reflected, to some in the growth in the number of applications of these technologically important metals. Given their increasing importance in application, high quality products of PGMs is required to meet the future demands [1]. The members of the platinum group metals (PGMs), viz platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os), form an important group of elements of increasing usage in the technologically developing world. Platinum was first discovered in the sixteen century in the Choco District of Columbia [2].

Palladium, rhodium, osmium and iridium were also discovered in 1803, some three hundred years after platinum. The last member of the platinum group metals to be discovered was ruthenium. The platinum group metals are amongst the 90 or so elements that comprise less than 2% by weight of the earth's crust or 10 miles thick outer layer of the earth. The platinum group metals platinum, palladium, rhodium, iridium, osmium and ruthenium together with silver and gold generally occur in nature associated with the major base metals iron, copper, nickel and cobalt and a wide range of minor elements such as lead, tellurium, selenium and arsenic. Technical and commercial considerations demand that the individual platinum group metals be separated from the other metals and from each other to high purity, with high yield and with a high percentage recovery[2].

Refining of platinum group metals consists of several physical and chemical stages, ore concentration by physical and chemical technique such as flotation, pyrometallurgical concentration producing copper-nickel sulphide matte and hydrometallurgical concentration and final refining to produce the individual platinum group metals [2]:

When the ore has been extracted from the mines, it is treated by a variety of processes which produces two products. The first is the "A mineral" which contains 30-40 per cent platinum group metals. The second is a much richer product containing 60 per cent platinum group metals, which is known as "Final Concentrate"[2]. The property that is common to all these platinum group metals is their noble character, owing to their passivity before chemical reagents

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[3].

Platinum, palladium and rhodium are the three principal metals of the platinum group, in the economic and commercial context. Currently, their main application is catalytic processes, and this characteristic has justified many studies on their recovery. The major demands and uses of Pt, Pd and Rh are indicated in figure 1 and figure 2. The PGM find varied applications in many very different fields. While gold is the traditional metal for jewellery, the use of platinum has benefited from the new fashion awareness. Palladium is applied as an alloying component and as a whitening agent in jewellery [3].

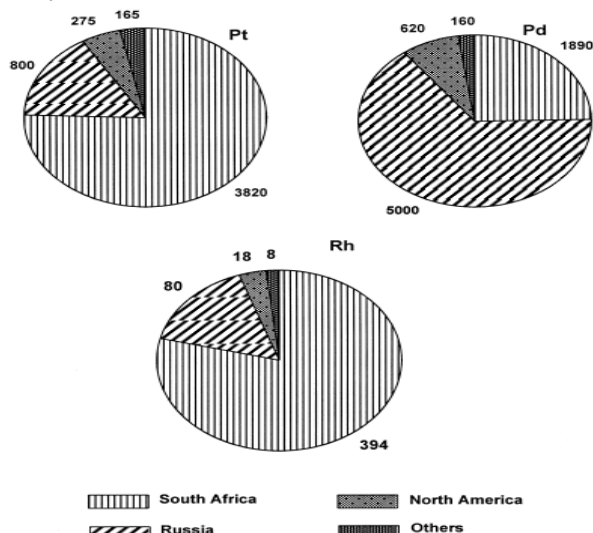


Fig. 1 Major producers of Pt, Pd and Rh (in 10<sup>3</sup> oz) [1].

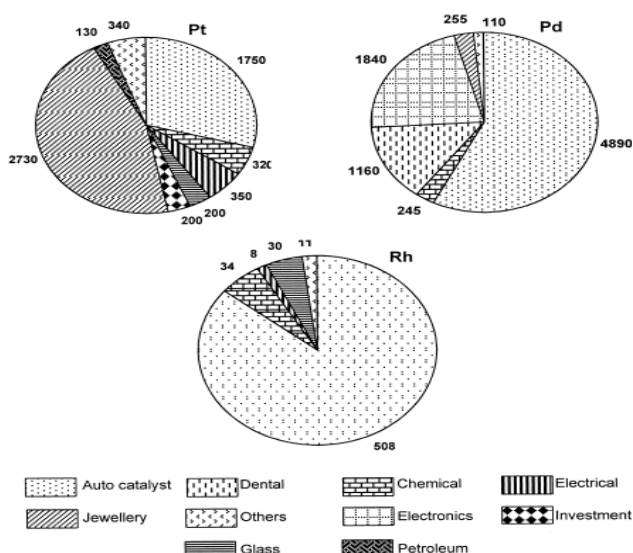


Fig. 2 Demand of Pt, Pd and Rh (in 10<sup>3</sup> oz) [1].

The automobile industry is the major consumer of PGM. Pt, Pd and Rh are used in automobiles as catalysts for the purpose of reducing levels of carbon monoxide, unburnt hydrocarbons

and nitrogen oxides in the exhaust gases. Typically an automobile catalytic converter contains 0.08% Pt, 0.04% Pd and 0.005-0.007% Rh supported on a base metal [3].

## II. PGM REFINING

Natural PGMs deposits are almost always related to base igneous rocks and are closely associated with copper, nickel and iron sulfides. The concentration of PGMs in these ores differ quite markedly depending on the origin and this has a significant bearing on the manner in which they are refined. In Canada, for instance PGMs are refined as a by-product of Cu-Ni refining due to their relatively small abundance. In South Africa, on the other hand PGM are mined as the primary product and Cu, Ni and Co are treated as by-products [1].

In the South African deposits the concentration is still less than 10g t<sup>-1</sup> ore and a number of physical and pyrometallurgical processes are required to concentrate the PGM. An outline of a typical process that has been used to concentrate PGM from South Africa ores is presented in figure 3 [1].

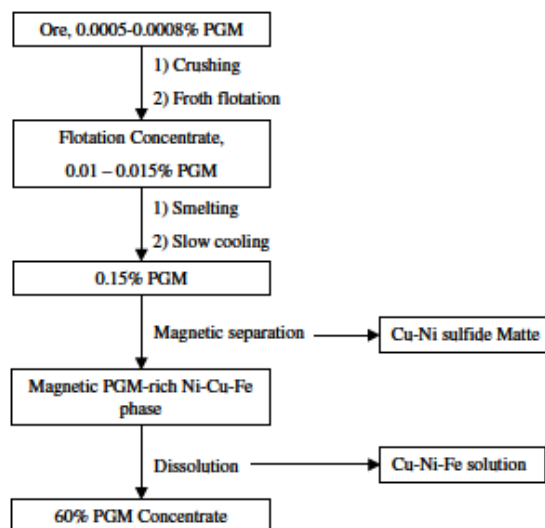


Fig. 3 Concentration process for PGMs from sulphide ores [1].

## III. CHLORO-COMPLEXES

Like other transition metals PGMs form numerous complexes with a variety of different ligands. The PGM-chloro complexes are well studied and important, as aqueous chloride solution is the only cost-effective medium in which all the PGMs can be brought into solution and concentrated. All the PGM in their tetravalent oxidation state form hexachloro complex anions predominantly in strong chloride media. The ammonium salts of the trivalent species are more soluble than the tetra valent hexachloro species and therefore selective precipitation of the tetravalent species is possible[1].

## IV. REFINING METHODS

In recent decades, several processes have been developed to recover and separate platinum group metals from synthetic or

industrial effluents, namely sorption, ion exchange, liquid-liquid extraction and related processes, impregnated resins and liquid membranes. These are powerful techniques that may involve environmental drawbacks such as release of solvent or extractant traces. Furthermore, their technical and economical efficiencies are limited by the treatment of dilute effluents [4]-[6].

A wide range of sorbents or ion exchange systems are available for platinum group metals recovery. Metals can be recovered by elution using different extractants. Alternatively, recovery can be also performed by the combustion and elimination of the organic sorbent, with resulting combustion products which are less hazardous to the environment than those of conventional ion-exchange resins.

Chitosan results from the alkaline deacetylation of chitin, the most abundant biopolymer in nature after cellulose. It is an aminopolysaccharide made up of both glucosamine and acetylglucosamine moieties. It is soluble in dilute mineral and organic acid solutions (except sulphuric acid and to a lesser extent phosphoric acid). Most industrial effluents containing platinum group metals are strongly acidic and chitosan can be used for these metals recovery only after a cross linking step to increase its chemical stability. Several chemical cross linking agents have been proposed, such as epichlorohydrin or glutaraldehyde. In the present work, glutaraldehyde has been selected for chemical stabilization [7].

Precious metals in their most common states tend to form the most stable complexes with ligands which contain donor atoms and are bound preferentially to soft bases. However precious metals can easily form complexes with chloride anions, and owing to the fact that the majority of processes that are used in hydrometallurgy involve the use of HCl, the metals are found in solution as chloro complexes. In such experimental conditions, nitrogen –containing sites may be protonated and bind hydrochloric moieties, forming carbocations, with which metallic anions may react with ion-exchange mechanism as suggested in the following reaction in the case of the anion tetrachloropalladate. Depending on the species of metal, the mechanisms of sorption or ion-exchange can compete or co-exist, and both hypotheses will be examined [8]-[10].

The platinum group metals, which are included in group VIII of the periodic table, have different chemical behaviour from the other elements of the group: Fe, Co and Ni. Their metallic properties are such as to suggest classification in pairs: Ru/Os, Rh/Ir, Pd/Pt. At the same time these elements are usually subdivided into two different groups: metals of the primary group, which comprise platinum and palladium, and the remaining elements of the group, which form the secondary PGMs. This classification comes from the fact that with conventional hydrometallurgical methods, the treatment of concentrates of precious metals is carried out by means of lixiviation with aqua regia, which yields a first separation into a soluble part and an insoluble residue. The soluble metals are gold and the metals of the primary platinum group and the insoluble ones are silver and the secondary PGM [11]-[12].

The growing demand for highly pure precious metals to use in high-tech applications, the need for modern and clean processes and the increasing volume of low grade PGM from secondary sources available for recycling, is having a direct impact today on the industrial practice of recovering and refining precious metals. Currently, solvent extraction is widely practiced in hydrometallurgy. It was during the 60s that effective extractant became commercially available and made possible the industrial expansion of the process. Since that time extensive research has been carried out which has led to the development of several new selective extractants, but parallel to this, new techniques has been proposed for the recovery of the precious metals. Some of these techniques are related to solvent extraction and others to the research of new more selective adsorbents for these metals [13]-[15].

The variety of processes used in the recovery and refining of precious metals can be classified into two major group process categories. These are based on the differences in the raw material sources on for example those obtained from mined platinum-bearing copper-nickel sulphide ores and the other from secondary raw material sources such as recycled industrial products. Examples of the latter include spent catalysts, electronic scrap, spent electrolytes, and jewellery scrap.

After the platinum group metals have been dissolved, the individual metals must be recovered. Depending on the raw material, the solution may contain all or some of the PGM, together with gold, silver and base metals. Numerous separation processes have been developed and used. In general, coarse separation is followed by a purification stage. The process used for coarse separation is determined largely by the composition of starting solution and the purification process depends on the particular PGM. The purification stage is necessary because, with few exceptions, an individual platinum group metal of commercially acceptable purity cannot be isolated from complex solutions in a single step.

The most important separation processes today make use of various combinations of precipitation, crystallization; distillation and solvent extraction. Some of the techniques mentioned in this section have current industrial applications, as well as those mentioned above and others are considered to be emerging technologies [15]. The precipitation and solvent extraction methods that are currently employed for the separation of PGM are explained in details in the following section.

#### V. PRECIPITATION METHOD

Precipitation is the basic process that has been used for the separation of the largest quantities of platinum group metals since the beginning of separation technology-precipitation crystallization of ammonium hexachloro complexes  $(\text{NH}_4)_2\text{Pt}_6$ . The process can be optimized in many ways by influencing solubilities (e.g., by valence changes, addition of a common ion, or changing the temperature and rate of precipitation).

The first step in separation of platinum is usually to precipitate platinum as  $(\text{NH}_4)_2\text{PtCl}_6$ . If the dissolved platinum is present as Pt(II), it must first be oxidized to Pt(IV), e.g. by chlorine. Excess dissolved chlorine is driven off by boiling, which also causes the palladium that had been oxidized to Pd(IV) to be reduced to Pd(II), for example with iron(II) salts or ascorbic acid. The ammonium hexachloroplatinate (IV) is precipitated preferably by slow addition of concentrated ammonium chloride solution at room temperature with stirring. The hydrochloric acid concentrated should be 1M, and the platinum content should be 50-200g/L [16].

#### VI. SOLVENT EXTRACTION METHOD

Solvent extraction also known as liquid-liquid extraction involves the distribution components between two immiscible phases, aqueous and organic, usually with chemical reaction. The organic phase is a solution containing a lipophilic extractant which forms complexes with the metal ion existing in the aqueous solutions which are transferred to the organic phase. The reaction is reversible, therefore by changing the chemical conditions the metal transfer from the organic phase to the aqueous phase [16].

The variety of chemical species that can be treated by solvent extraction methods is greater than those by other methods such as precipitation or ion exchange, and thus the number of solvent extraction systems which can be employed for a certain purpose is much greater than that of these other methods. This advantage of solvent extraction is especially marked with precious metals, because they easily form species which are extractable into an organic phase with various reagents. Moreover, the relatively high cost of reagents and of the recovery and storage of organic solvents during the solvent extraction process could be outweighed by the value of the precious metals thus produced.

The use of solvent extraction technology to replace traditional processes has been the subject of considerable research and development effort since the 1970s. This newer technique has been used commercially as of 1995 in at least three of the principal refineries [2, 16].

The principle of solvent extraction in refining is as follows: when a dilute aqueous metal solution is contacted with a suitable extractant, often an amine or oxime, dissolved in a water-immiscible organic solvent, the metal ion is complexed by the extractant and becomes preferentially soluble in the organic phase.

The organic and aqueous phases are then separated. By adding another aqueous component, the metal ions can be stripped back into the aqueous phase and hence recovered. Upon the identification of suitable extractants, and using a multistage process, solvent extraction can be used to extract individual metals from a mixture. Solvent extraction is a relatively high cost process, owing to the specialty organic extractants required and the expenses of recovery and storage of organic solvents. However, in a precious-metal recovery operation, these costs are easily outweighed by the increased

efficiency and PGM recovery as well as shortened metal-in-process time [2, 16].

All solvent extraction processes are based on the chloro complexes of the PGM, as chloride is the only effective medium by which the PGM can be brought into solution. Selection of suitable extractants utilizes specs of the aqueous chemistry of the metal species, such as the nature of the complex ionic species and most stable PGM complexes are those having heavier donor atoms. The raw precious metal concentrate is totally dissolved in hydrochloric acid-chlorine solution to form the soluble chloride ions of each of the metals. Silver remains as insoluble silver chloride and can be filtered off.

Base metals are also extracted in this step, and are removed from the organic phase by scrubbing with dilute hydrochloric acid. Iron powder is then used to reduce the gold species and recover them from the organic phase. Many liquid-liquid extraction systems have been described that can be used for solvent extraction of metals. Much research into the platinum group metals has been carried out, mainly aimed at their separation.

The extraction process does not usually involve a distribution of the extractable compounds between the organic and the aqueous phases. More often, the extractable compounds are dissolved in an inert organic phase. The system is generally diluted with an inert solvent to lower the viscosity. Solvent extraction is often characterized by distribution coefficients that vary greatly from element to element. These can usually be modified by chemical methods to give conditions favorable for the separation of PGMs [17].

However, the separation factors resulting from the ratios of the distribution coefficients rarely enable a single separation stage to provide purities that fulfill modern requirement for metal quality. Although separations are generally better than those affected by precipitation crystallization, coarse separation by solvent extraction must be followed by purification. Trioctylamine is used widely for the solvent extraction of large amounts of platinum from refinery solutions and it is also used for the solvent extraction. Stripping can be facilitated by changing the stripping solution or the valence of the metal. Diluent solvents are employed when carrying out solvent extraction with amines [18].

#### VII. CHEMISTRY OF PLATINUM GROUP METALS SEPARATION

*Dissolution Properties* Differences in reactivity toward chemical reagents, especially oxidizing acids and molten salts, can often be utilized for coarse separation of platinum group metals. The main strong oxidizing conditions used in the industry for solubilization of PGM feed stocks consist of aqua-regia treatment. Aqua-regia leaching is slowly being phased out in preference for the more efficient wet chlorination technique, in which the leaching agent is hydrochloric acid, with the addition of chlorine to increase the solution's oxidation potential. In addition, the  $\text{HCl}/\text{H}_2\text{O}_2$  lixiviant combination is a common variant [2, 16].

**Solution Equilibria** In the crystallization process (by either evaporation or precipitation), the solubilities of chloro-complexes of the platinum group metal are very important, as is the possibility of altering these solubilities. The temperature dependence of these solubilities is generally quite large and can be considered at many stages of the processes. An even more useful phenomenon in separation technology is the effect on solubility of the addition of a common ion, which is utilized in precipitation crystallization. Solubility can usually be varied over two orders of magnitude. The solubility of AgCl is affected not only by the concentration of the acid, but also by that of  $H_2PtCl_6$  [16].

**Redox Reactions and Stability of Complexes:** The precious metals show a wide variety of oxidation states. Many separations are made possible by valence changes in redox systems. This applies mainly to precipitation crystallization, but also to solvent extraction and distillation. In practice, the kinetic and thermal stabilities of the valences in complexes are important, as is the redox stability. The platinum group metal complexes formed vary considerably with the oxidation state. Whereas the majority of PGMs form full chloro complexes, the trivalent metals form mixtures of chloroaquo species in equilibrium with each other that are very dependent on the total chloride concentration. Chloro complexes differ in the greater or lesser degree of ease with which they can show substitution reactions [16].

**Reduction to metal:** Since PGMs are all electrochemically noble metals, selective reduction and cementation by base metal is not possible. In the past, collective cementation from aqueous solutions by zinc was often an important step, both for separation and for recovery of PGM from recycled solutions. However, the use of zinc as a cementation agent is not possible for environmental reasons. Where cementation cannot be avoided, iron, aluminium alloys can be used instead. In aqueous media, hydrazine, formate or boranate can be used to reductively precipitate elemental PGM.

## VIII. MATERIALS AND METHODS

### A. Samples

Platinum liquor was used for this study; this was the filtrate after all the impurities have been removed and was sampled for platinum analysis. The temperature of the platinum liquor was measured and the oxidizing agent was added to change the oxidation state of platinum. Ammonium chloride solution was then added to precipitate platinum. The final sample was taken to the laboratory for platinum analysis whereby a desired platinum concentration in the filtrate is less than 300 ppm.

### B. Equipments

The test work was carried out in a batch reactor, for the process of platinum precipitation. Acid totalizer was used to measure the concentration of HCl and the pH of the platinum liquor was checked to make sure that it was not too acidic as it hinders the chemical reactions.

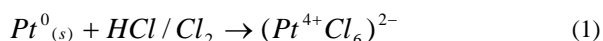
### C. Reagents

After the acidity of the liquor was checked, HCl or water was added. If total acid of the liquor was less than 2.5% HCl was added and if the acidity was more than 2.7% water was added to the platinum liquor. The pH of the platinum liquor was measured and monitored to range between 2–4 as this was established to be optimal pH for the reaction to occur.

Hydrogen peroxide was used as an oxidizing agent to change the oxidation state of platinum from  $Pt^{2+}$  to  $Pt^{4+}$  in order to be effectively precipitated. Ammonium chloride solution was added as a reducing agent to precipitate platinum. Wood flour was used to soften the platinum salts to help during the filtration of platinum as it enlarges the particles size of the platinum salts so that they cannot pass through during the filtration.

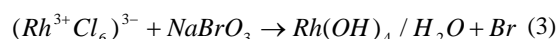
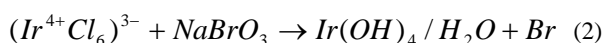
### D. Experimental procedure

Platinum was firstly dissolved in the presence of hydrochloric acid and chlorine gas as the oxidizing agent and the reaction that took place during the dissolution of platinum is as follows:



The dissolution of platinum took about 8 hours depending on the quantity of platinum loaded in the reactor. The dissolved platinum liquor in the form of  $H_2[PtCl_6]$  or  $H_2[PtCl_4]$  known as chloro-platinic acid (CPA) was obtained after filtration. This platinum liquor is very acidic and sodium hydroxide solution was used to adjust the pH so that reaction with other reagents can take place.

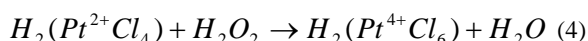
The dissolved liquor which is in the form of  $H_2[PtCl_6]$  was pumped to pH 8 hydrolysis stage for extraction of rhodium and iridium from platinum liquor. During the extraction of rhodium and iridium, sodium bromate solution ( $NaBrO_3$ ) was used as an oxidizing agent to oxidize rhodium and iridium. The reaction which took place during the addition of sodium bromate is as follows:



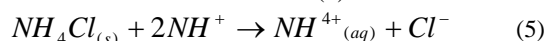
Sodium bromate was added until pH of 3, the temperature of the platinum liquor was increased to 100°C and sodium bicarbonate solution added until pH of 8 was achieved.

Sufficient amount of sodium bicarbonate was added to precipitate rhodium and iridium and liquor rich in platinum passed through as filtrate. Excessive addition of sodium bicarbonate is undesirable as it could lead to precipitation of platinum. The liquor which is rich in platinum was pumped to DMG stage where palladium is extracted by precipitation from platinum liquor using organic salts known as DMG. For the required specification after DMG addition, palladium should be less than 5ppm. The liquor in the form of  $Pt^{4+}Cl_6$  was filtered and pumped to next process stage where platinum is oxidized by hydrogen peroxide. Hydrogen peroxide was

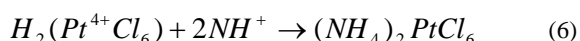
added until the redox potential was more than 700mV. The reaction that took place during the oxidation of platinum is as follows:



During this reaction in (4) a color change was observed, the process liquor turned into a yellow color. The residence time of 15 minutes was allowed and ammonium chloride solution was added to precipitate platinum. The ammonium chloride solution was prepared by dissolving ammonium flakes in water to form a solution as indicated in (5).



When ammonium chloride solution was added into the process liquor the following reaction occurs:



The reaction time of 30 minutes was allowed and the sample was taken to the laboratory for platinum analysis. The expected result was required to be less than 300ppm which was normally not achieved. On passing the process liquor was allowed to be dropped and filtered, the yellow platinum salts in the form of  $[NH_4]_2PtCl_6$  were kept in glove-box filter and prepared to be dug off, the platinum salts were mixed with water and pumped to the last process stage where platinum was reduced using hydrazine. The reduced platinum salts was dug-off and sent to ovens where platinum was burnt to release moisture and the final product which is platinum was obtained.

#### E. Data analysis

Data was analyzed using the LIMS program to determine the correlation between process variables and the significance of each process variable in the formation of platinum particles. The samples were analyzed using the LIMS program, for platinum. The samples were registered on the system where the volume of the platinum liquor in the reactor was recorded for accuracy of the results. The volume of the liquor was required to determine the quantity of platinum in filtrate solution. The instruments used for analysis of platinum were calibrated before analyzing samples. The minimum of three samples were taken for analysis to achieve consistency of results.

### IX. RESULTS AND DISCUSSION

Table 1 indicates the results prior and after the investigation. The amount of ammonium chloride used to precipitate platinum was not initially calculated. Temperature and the potential difference were also not controlled for the precipitation of platinum.

TABLE I  
PLATINUM CONCENTRATION IN THE EFFLUENT

Batch no.	Pt(ppm)-effluent	T (°C)	V (mV)	Target t	pH
1	921	45	160	300	1
2	891	55	160	300	1.3
3	975	55	160	300	1.5
4	830	55	160	300	1.4
5	218	64	200	300	3.5
6	180	62	200	300	2.9
7	250	62	200	300	3.4
8	116	65	200	300	3.8

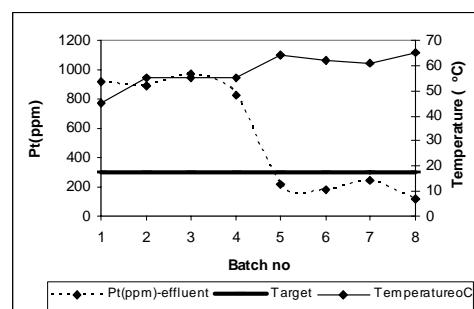


Fig. 4 Platinum concentration in effluent vs. temperature

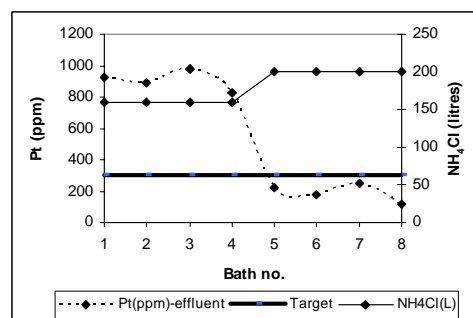


Fig. 5 Platinum concentration in effluent vs. ammonium chloride

Fig 3 shows the platinum concentration in the effluent and the temperature in the 8 batches treated. The platinum concentration in effluent indicates the efficiency of the platinum precipitation process and it is desired to be less than 300 ppm and it was very high at 975 ppm. This was the results obtained prior the investigation and monitoring and adjustment of temperature. At temperature above 50°C the target of less than 300 ppm platinum in the effluent was reached.

The amount of ammonium chloride for platinum precipitation was also increased from 160 L to 200 L. In fig 4, when the amount of ammonium chloride was increased the platinum in the effluent dropped to the desired value of less than 300 ppm, due to the sufficient amount added to precipitate the maximum amount of platinum in the liquor.



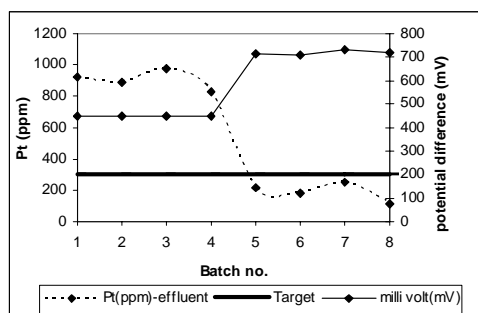


Fig. 6 Platinum concentration in effluent vs. redox potential

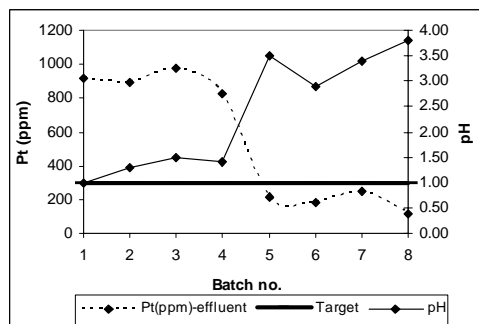


Fig. 7 Platinum concentration in effluent vs. pH

Redox difference is one of the critical parameters on the platinum precipitation process. The platinum complex  $\text{Pt}^{4+}\text{Cl}_6$  is desired as it is more stable than  $\text{Pt}^{2+}\text{Cl}_6$  complex. Higher redox difference indicates the formation of  $\text{Pt}^{4+}\text{Cl}_6$  complex, the value of redox difference is proportional to the oxidation of  $\text{Pt}^{2+}\text{Cl}_6$ , and the redox potential was monitored and controlled above 700mV. The total acid of the platinum liquor was adjusted to pH that ranges between 2 -4.

#### X. CONCLUSION

This work has demonstrated that temperature at which ammonium chloride is added for platinum precipitation has a great effect on the platinum content reporting to the effluent. When temperature was increased the platinum in the effluent was reduced dramatically because the platinum complexes formed were more stable and reacted effectively with the reducing agent.

The amount of ammonium chloride had influenced the platinum precipitation process; sufficient ammonium chloride for the effective platinum precipitation was calculated prior addition. The redox potential was increase by the addition of hydrogen peroxide until it was more than 700 mV. For effective platinum precipitation the platinum complex  $\text{Pt}^{2+}$  was changed to  $\text{Pt}^{4+}$  by addition of hydrogen peroxide.

The total acid of platinum liquor was adjusted to pH ranging between 2 -4. The total acid strength was adjusted to 2.5-2.7% using HCL and water for dilution. The required pass specification of platinum salt content less than 300 ppm was achieved as the three critical parameters that play an important role during precipitation were controlled. Further work is

recommended to investigate the optimum condition for the different parameters.

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