LEACHING OF SELECTED PGMs:
A THERMODYNAMIC AND ELECTROCHEMICAL STUDY
EMPLOYING LESS AGGRESSIVE LIXIVIANTS

by

R.J. Kriek

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CONTENTS

Abstract

Historically the platinum group metals (PGMs) have been, and are still being dissolved by means of rather aggressive methods, e.g. aqua regia. Limited research has been conducted into the dissolution of the PGMs using different oxidizing agents. The dissolution of gold on the other hand has been afforded extensive research, and numerous papers and review articles have been published on the subject. The last number of years has seen the biggest application by volume of the PGMs as part of autocatalysts towards the degradation of harmful motor vehicle exhaust gases. This has subsequently sparked research into the recovery of specifically platinum, palladium, and rhodium from spent autocatalysts. Currently pyrometallurgical recovery of PGMs is being employed predominantly. A hydrometallurgical process on the other hand is, based on current technology, still a rather aggressive process that makes for high maintenance costs and an unpleasant environment. Gold has traditionally been dissolved by making use of cyanide, which is still the major route for gold dissolution. Due to environmental concerns lixiviants such as thiosulphate ($S_2O_3^{2-}$), thiourea (H_2NCSNH_2), and thiocyanate (SCN^-) are gaining acceptance due to them being more environmentally friendly and giving good recoveries. These 'softer' alternatives have however not been tested on the PGMs. It is therefore the aim of this study to obtain an improved understanding of the leaching of the PGMs using lixiviants less aggressive than aqua-regia. These lixiviants include (i) SCN^-, (ii) $S_2O_3^{2-}$, (iii) H_2NCSNH_2, and (iv) $AlCl_3$/HCl.

A thermodynamic study highlighted the fact that thermodynamic data for platinum-, palladium- and rhodium complexes are basically non-existent. To therefore obtain a clearer thermodynamic understanding of the leaching of the platinum group metals by means of these alternative lixiviants, future detailed speciation and thermodynamic investigations need to be conducted.

An exploratory electrochemical investigation focusing on open circuit potentials and potentiodynamic scans, showed $AlCl_3$ / HCl / NaOCl to be a good candidate for the leaching of the platinum group metals followed by SCN^- / Fe^{3+} and $CS(NH_2)_2$ / Fe^{3+}.

Actual leach results, employing virgin autocatalysts as sample material, again highlighted the potential of $AlCl_3$ / HCl / NaOCl as being a good lixiviant system. The surprise package, however, has been SCN^- / Fe^{3+} that rendered very good results for Pd and Pt.

Keywords

Leaching, Lixiviant(s), Platinum, Palladium, Rhodium, PGM (Platinum Group Metal), Catalytic Converter / Autocatalyst, Thermodynamics, Electrochemistry

Objectives

This project has two main objectives, i.e. an academic objective as well as a strategic objective:

- Academic Objective

  To obtain an improved understanding of the leaching of the PGMs using lixiviants less aggressive than aqua-regia. These lixiviants will include (i) thiocyanate (SCN^-), (ii) thiosulphate ($S_2O_3^{2-}$), (iii) thiourea (H_2NCSNH_2), and (iv) $AlCl_3$/HCl. The choice of these specific lixiviants has, to some extent, followed from the literature review that was conducted. Virgin autocatalysts will be used as sample material.

- Strategic Objective

  To work towards the development of a leaching method for the PGMs, that is less aggressive than the aqua-regia method, which can be employed as part of a hydrometallurgical process for the recovery of PGMs from spent catalytic converters.

Methodology

The methodology for conducting this project can be divided into three sections, i.e. (a) a literature review, (b) a desk / computer study, and (c) and experimental section. To some extent the chronological order as depicted in figure 12 will be followed. The desk / computer study is in essence a study of the thermodynamics of the different lixiviant systems with regard to platinum, palladium and rhodium respectively. The experimental section will consist of electrochemical investigations and leaching experiments.

- Literature Review
  A literature review will be conducted so as to identify the different lixiviants that have already been investigated with regard to their capacity to oxidize/dissolve PGMs irrespective of the sample material used, i.e. be it a PGM ore, autocatalysts, the metal itself, etc.

- Selection of Lixiviants
  Resulting from the literature review a selection will be made of the different lixiviants that will be investigated with regard to their capacity to oxidize/dissolve a specific PGM.

- Thermodynamic Study
  A software package, HSC 5.1, developed by Outokumpu, will be used to determine the thermodynamic stability regions of the individual PGM species in respect of the specific lixiviant that is employed.

- Electrochemical Investigation
  Employing a potentiostat equipped with a rotating disc working electrode (manufactured with the specific metal to be investigated), the rest potential (mixed potential) of the PGM-lixiviant system will be determined and a potentio-dynamic scan will be conducted across a predetermined potential range. The rest potential will give an indication as to the potential degree of dissolution/oxidation of a specific PGM by a specific lixiviant relative to other lixiviants. This, however, does not convey anything about the kinetics of dissolution. The potentio-dynamic scan, i.e. current-flow versus potential, conveys the kinetics of the dissolution process as it measures the current-flow per unit area (e.g. $A.cm^{-2}$) at a specific applied potential (V).

- Leaching Experiments

  Leaching experiments will be conducted in a single stirred reactor as well as in a fluidized bed reactor. Analysis of the leach liquor will be conducted by means of an inductively coupled plasma (ICP) mass spectrometer.

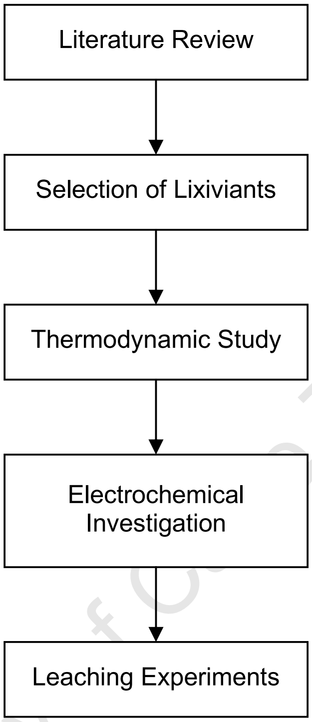


Fig i Methodology for conducting this project.

Chapter 1

BACKGROUND

It goes without saying that the PGMs are valuable commodities. In general the price of platinum can be taken as almost double that of gold, the price of palladium as half that of gold, and the price of rhodium as six times that of gold. PGMs have found a number of uses and research is underway to identify new applications for these noble metals. This includes the current drive to use PGMs in fuel cells, which hopefully will assist in replacing fossil fuels as an energy source. Platinum has found a great demand from the jewellery industry, but as can be seen from figure 1 the demand for jewellery as of 1999 seems to be declining. The demand for platinum to be used in autocatalyst, on the other hand, has shown an increase as of 1999, and as of 2003 has surpassed jewellery as the greatest user of platinum.

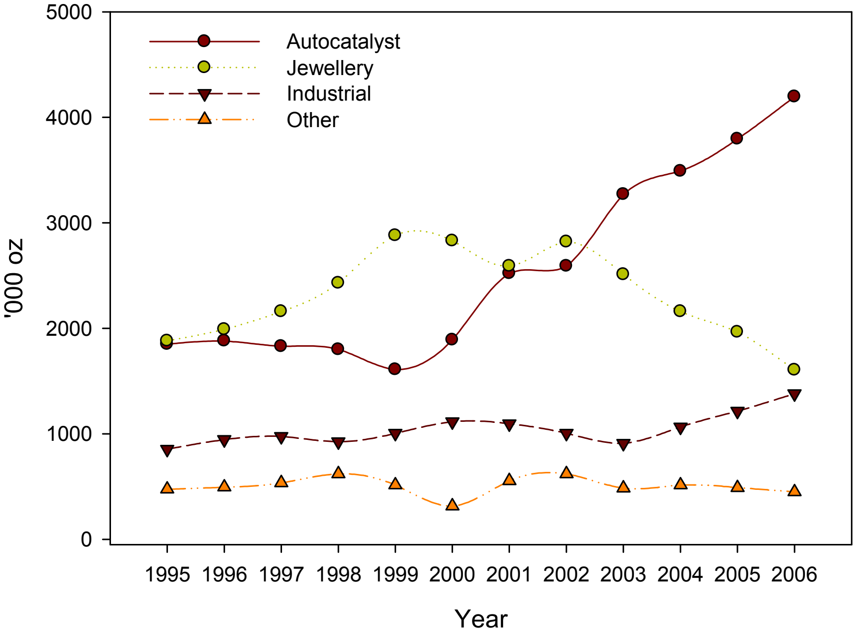


Fig 1 Platinum demand by application from 1995 to 2006[1].

From an ounce per ounce basis, there has been historically a greater demand for palladium, but platinum has caught up in the last few years. It has not found such a great usage in the jewellery industry, but has found a number of industrial applications. These applications include chemical, dental, and electronics. Palladium, as can be seen from figure 2, has played a dominant role in autocatalysts as of 1998.

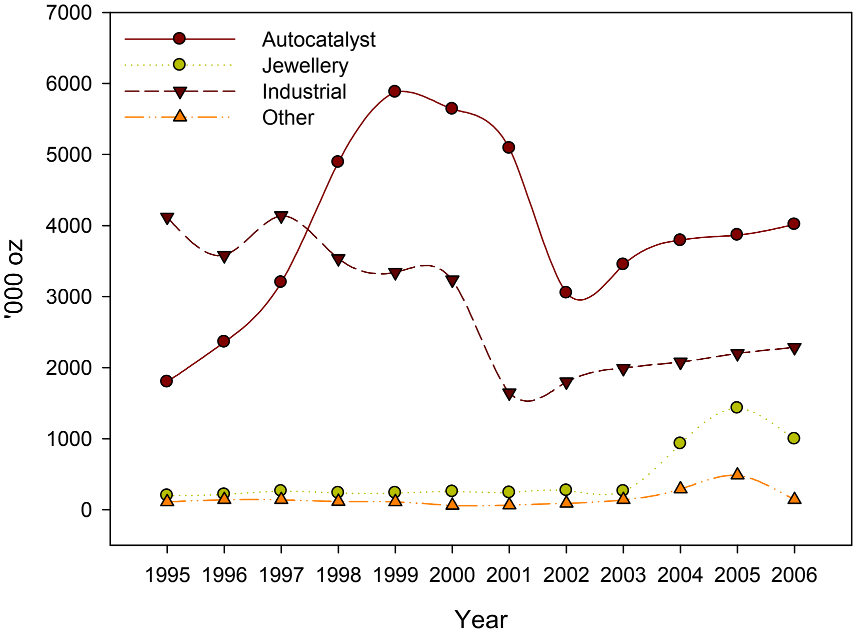


Fig 2 Palladium demand by application from 1995 to 2006[1].

Rhodium has not found as many uses and there has not been as big a demand for the metal. From figure 3 it can be seen that it is predominantly used in autocatalysts, and it seems to be increasing.

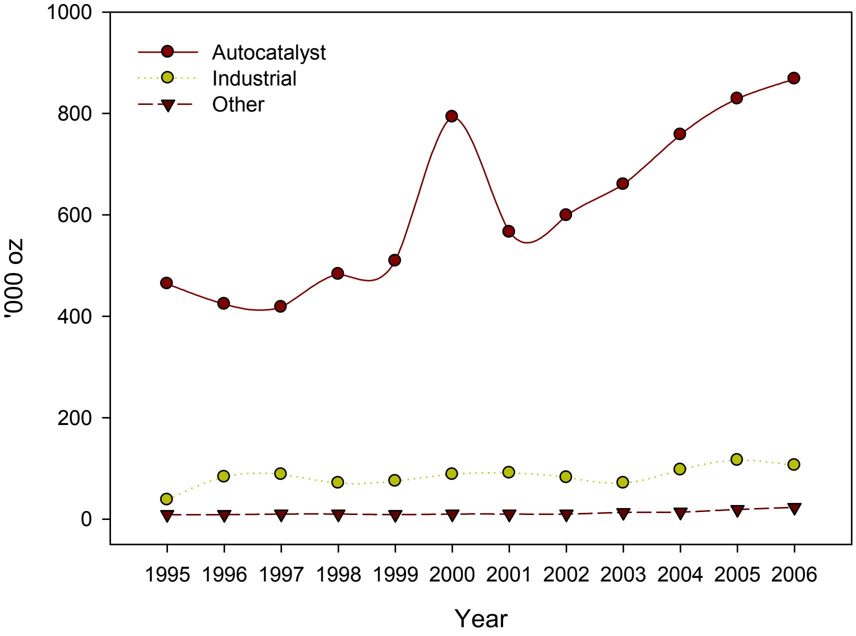


Fig 3 Rhodium demand by application from 1995 to 2006[1].

South Africa's Bushveld Complex consists of three reefs. The Merensky reef typically has a PGM ore grade of 3.43 g/t platinum, 1.98 g/t palladium, and 0.19 g/t rhodium. The Upper Group 2 (UG2) reefs typically has a PGM ore grade of 2.66 g/t platinum, 1.71 g/t palladium, and 0.44 g/t rhodium, whereas the Plat reef is more variable with total PGM content varying between 7 and 27 grams per tonne[2]. It has been hinted that the average total PGM loading on the honeycomb substrate is in the order of 2g PGM per kg of substrate. That translates to a total PGM content of 2000 grams per tonne compared to a total ore content of between 4 and 27 grams per tonne. This makes spent autocatalysts an extremely attractive secondary source of PGMs. From figure 4 it is clear that the recovery of PGMs from spent autocatalysts is increasing on a year by year basis. In 2006 the PGMs recovered from spent autocatalysts as a percentage of the PGMs used in the manufacture of new catalysts were as follows: Pt (20%), Pd (20%), and Rh (20%).

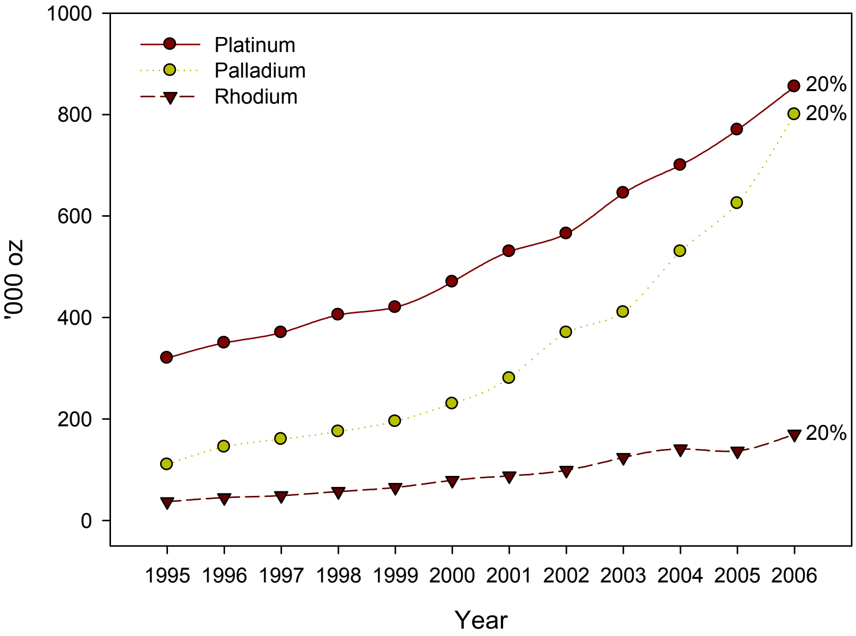


Fig 4 Recovery of PGMs from spent autocatalysts[1].

Apart from autocatalysts containing PGMs, catalysts for petroleum cracking, dehydrogenation, reforming, and hydrogenation, contain platinum and palladium (amongst other metals), and are extensively used in the refining and petrochemical industries. These spent catalysts are considered to be environmentally hazardous as they contain contaminants such as coke, vanadium, and nickel to name but a few[3]. These industrial catalysts and autocatalysts, in the spent form, are excellent secondary sources of platinum group metals (PGMs) as they contain these metals in considerably higher concentrations than the ores from which they are extracted[4,5], as mentioned above.

Chapter 2

LITERATURE REVIEW

PGMs can be recovered from spent catalysts by means of wet methods (hydrometallurgical), dry methods (pyrometallurgical), or electrochemical methods[3]. Currently pyrometallurgy is still primarily being used, be it for the recovery of PGMs from ores or spent catalysts[6]. A study by Hoffmann[7,8] in 1988, comparing PGM recoveries from different processes, has concluded that the pyrometallurgical recovery of rhodium in copper smelters is the most advantageous, and can be as high as 90-95%, while other authors contend that pyrometallurgy gives lower recoveries presumably due to the high melting points of the alumina substrates[9]. To this day, however, smelting is still extensively used as part of the processing of Platinum Group Metal (PGM) ores by companies such as Anglo Platinum, Impala Platinum, and Lonmin. Smelting does have its own set of associated problems, e.g. it is energy consuming and results in extensive air pollution. It is therefore by no means of the imagination an environmentally friendly process. In personal discussions with the then MD of Lonmin's Western Platinum Refinery in Brakpan, South Africa, Dr Francesca Lessing[10], as well as the R&D Manager of Impala Platinum's Refinery in Springs, South Africa, Mr Eduardo Orelano[11], it was quite clear that if smelting (pyrometallurgy) can be replaced with an all hydrometallurgical process, they would welcome it. Currently a company by the name of A1, which collects spent catalytic converters mainly in the United States, supplies Impala Platinum with these converters, which feeds it to their smelters producing a collected matte phase.

In applying a hydrometallurgical route, the PGMs are separated from the catalyst surface either by means of (a) PGM dissolution, or (b) substrate dissolution[9]. In the first instance the PGMs are dissolved leaving the bulk of the substrate unaffected. Unfortunately, this only holds for α-alumina to a large extent as it is relatively insoluble; γ-alumina on the other hand is relatively easily dissolved[9]. This would require the conversion of γ-alumina to α-alumina at 1500°C prior to dissolution. In the latter case, the substrate is dissolved leaving the PGMs as an insoluble sludge. The substrate dissolution process requires large amounts of reagents and poses severe environmental problems relating to waste disposal if the solution is not recycled back to alumina[4,12]. This has then also left the PGMs as an insoluble sludge, which requires subsequent dissolution and treatment. From an economic and environmental point of view this would clearly not be the way to go.

The standard reduction potentials, E° values, at 298.15 K (25°C), and at a pressure of 101.325 kPa (1 atm), of platinum, palladium and rhodium, are as follows[57]:

$$\mathrm{Pt}^{2+} + 2e^{-} \rightarrow \mathrm{Pt} \qquad (E^{\circ} = 1.118\mathrm{V}) \qquad \ldots 1$$

$$\mathrm{Pd}^{2+} + 2e^{-} \rightarrow \mathrm{Pd} \qquad (E^{\circ} = 0.951\mathrm{V}) \qquad \ldots 2$$

$$\mathrm{Rh}^{3+} + 3e^{-} \rightarrow \mathrm{Rh} \qquad (E^{\circ} = 0.758\mathrm{V}) \qquad \ldots 3$$

Wu[13], investigating the recovery of precious metals from automotive catalytic converters, points out that the dissolution of PGMs is governed by, e.g., the following redox reactions depending on the lixiviant that is used (in this case HCl)[12]:

$$\mathrm{Pt} + 4\mathrm{Cl}^{-} \rightarrow \mathrm{PtCl_4}^{2-} + 2e^{-} \qquad (E^{\circ} = -0.73\mathrm{V}) \qquad \ldots 1$$

$$\mathrm{PtCl_4}^{2-} + 2\mathrm{Cl}^{-} \rightarrow \mathrm{PtCl_6}^{2-} + 2e^{-} \qquad (E^{\circ} = -0.74\mathrm{V}) \qquad \ldots 2$$

$$\mathrm{Pd} + 4\mathrm{Cl}^{-} \rightarrow \mathrm{PdCl_4}^{2-} + 2e^{-} \qquad (E^{\circ} = -0.62\mathrm{V}) \qquad \ldots 3$$

$$\mathrm{PdCl_4}^{2-} + 2\mathrm{Cl}^{-} \rightarrow \mathrm{PdCl_6}^{2-} + 2e^{-} \qquad (E^{\circ} = -1.29\mathrm{V}) \qquad \ldots 4$$

$$\mathrm{Rh} + 6\mathrm{Cl}^{-} \rightarrow \mathrm{RhCl_6}^{3-} + 3e^{-} \qquad (E^{\circ} = -0.44\mathrm{V}) \qquad \ldots 5$$

The associated conditions of a specific leach solution, i.e. ligand concentration, the PGM complex that can be formed, and therefore the corresponding standard potentials that can be achieved, will determine whether or not leaching will occur and the extent thereof.

The most stable chloride complexes are $\mathrm{PtCl_6}^{2-}$, $\mathrm{PdCl_4}^{2-}$, and $\mathrm{RhCl_6}^{3-}$. All of the above-mentioned reactions therefore have to occur. A standard potential higher than 0.74V is therefore required to oxidise a mixture of Pt(s), Pd(s), and Rh(s). In *aqua regia* for example the corresponding reduction reactions are[12]:

$$2\mathrm{NO_3}^{-} + 4\mathrm{H}^{+} + 2e^{-} \rightarrow \mathrm{N_2O_2} + 2\mathrm{H_2O} \qquad (E^{\circ} = 0.81\mathrm{V}) \qquad \ldots 6$$

$$\mathrm{NO_3}^{-} + 3\mathrm{H}^{+} + 2e^{-} \rightarrow \mathrm{HNO_2} + \mathrm{H_2O} \qquad (E^{\circ} = 0.94\mathrm{V}) \qquad \ldots 7$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \qquad (E^\circ = 0.96V) \qquad \ldots 8$$

Oxidation of Pt(s), Pd(s), and Rh(s), in a chloride medium, will therefore occur as the potentials of the reduction reactions are high enough.

It is important to take into account the speciation of the PGM complexes in a specific solution, i.e. the PGM complexes that can be formed given the ligand concentration in solution. D'Aniello[15] has postulated that Pt and Pd chloride complexes may hydrolyse to create hydroxo complexes, and to prevent hydrolysis high chloride concentrations and a pH less than unity has to be maintained.

Mishra[14] listed the standard reduction potentials of a few commonly used oxidants, and as can be seen each of them should be able to oxidise Pt(s), Pd(s), and Rh(s) provided the kinetics is favourable.

$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O \qquad (E^\circ = 1.45V) \qquad \ldots 9$$

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad (E^\circ = 1.49V) \qquad \ldots 10$$

$$Cl_2(g) + 2e^- \rightarrow 2Cl^- \qquad (E^\circ = 1.35V) \qquad \ldots 11$$

$$Br_2 + 2e^- \rightarrow 2Br^- \qquad (E^\circ = 1.09V) \qquad \ldots 12$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad (E^\circ = 1.77V) \qquad \ldots 13$$

$$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O \qquad (E^\circ = 1.44V) \qquad \ldots 14$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \qquad (E^\circ = 0.96V) \qquad \ldots 15$$

Because of the possible presence of oxidisable impurities, e.g. Pb^{2+}, Mn^+, S^{2-}, etc., more oxidant could be required for the dissolution of specific PGMs above the stoichiometric amount. Furthermore, oxidising agents with $E^\circ > 1.23V$ will result in the oxidation of water, which will lower the amount of oxidant available for PGM dissolution[13,14,15]. Oxidants with standard reduction potentials between 0.74V and 1.23V will therefore be strong enough to oxidise the PGM but not water[15].

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (E^\circ = -1.23V) \qquad \ldots 16$$

Ensuring the required concentration of the desired ligand, e.g. Cl^-, an associated salt can be added to the solution. These might include, amongst others, NaCl, KCl, $FeCl_3$, and $AlCl_3$. It has been found that in the event of employing *aqua regia*, the addition of $AlCl_3$ will aid in decreasing gas evolution and HCl loss, thereby suppressing the dissolution of the alumina substrate[16].

In autocatalysts rhodium is prone to oxidation during use resulting in the formation of Rh_2O_3, which may resist dissolution[17]. Wu[13] pointed out that studies[18,19] have shown that Rh_2O_3 is for all extensive purposes insoluble in acid under oxidising conditions, unlike finely divided rhodium metal, which could account for the poor dissolution of rhodium (and other PGMs) from spent catalysts as the rhodium oxide on the surface of the particles acts as a protective layer inhibiting the dissolution of PGMs below. This would obviously require some sort of pre-treatment step, and as part of the above-mentioned study a hydrogen reduction step as a precursor to the leach resulted in the recovery of both platinum and rhodium in excess of 99%. D'Aniello[15], however, has found that it is not necessary to use prereduction methods so long as *aqua regia* is used as the leaching solution.

The two major leaching solution systems investigated by Wu[13] were (a) HCl + H_2O_2, and (b) HCl + HNO_3 (*Aqua Regia*). The effectiveness of the first system was improved with the addition of specific additives, i.e. H_2SO_4 and F^-, and was it found that the HCl (5.7N) + H_2SO_4 ($\geq$ 16.2%) + F^- (0.26%) + H_2O_2 (5-8% v/v of 30% w/w) system was as effective as the HCl + HNO_3 system, and in some cases even superior. The advantage of the H_2O_2 system is that no toxic vapours are produced compared to the *aqua regia* system.

With respect to particle size her study showed that the leaching rate, as well as the time required to reach the maximum leachate concentration, is not dependent on the particle size. In general it can be said that with smaller catalyst particle size, the interfacial area between the solids and liquids becomes greater, and the distance which the solute has to diffuse into the particle becomes smaller. It could therefore be expected that the rate of mass transfer would increase. However, the leaching rate is independent of the particle size implying that either the interfacial area is not increased, or the reaction kinetics are much slower than the mass transfer rate. Other authors have also concluded that PGM recoveries are not dependent on particle size[12,20,21,22]. It is furthermore noted that precious metals are present as a surface deposit, so that the extent of comminution should not be a critical parameter. In fact, with the goal of maximum precious metal dissolution with minimum substrate dissolution, it may well be a disadvantage to crush the catalyst, especially in the case of the acid-soluble γ-alumina[23].

An agitation speed of 400rpm was found to be optimum, above which it had no effect on leaching. The agitation speed of 400rpm was also found to be the minimum speed required at which all particles were well suspended.

It was found that for both platinum and palladium, increasing the leaching temperature significantly decreases the leaching time with palladium having a shorter effective leaching time. Leaching temperature, however, can not be raised too high because of side-reactions, higher pressures, corrosion, and possible PGM evaporation. The optimum temperature range was found to be between 70 and 90 °C.

It was however found that catalyst type is more important than leaching temperature and leaching time.

2.1 Aqua Regia (HCl / HNO_3)

It is well known that the best yield with regard to PGM recovery is achieved through the use of *aqua regia*, generally in the form of 3 to 4 parts of hydrochloric acid to 1 part nitric acid. In the case of platinum and palladium the following chemical reactions would be applicable[24]:

$$3Pt + 4HNO_3 + 18HCl \rightarrow 3H_2PtCl_6 + 4NO + 8H_2O \qquad \ldots 17$$

$$3Pd + 2HNO_3 + 12HCl \rightarrow 3H_2PdCl_4 + 2NO + 4H_2O \qquad \ldots 18$$

Apart from the good yield achieved, the high concentration of hydrochloric acid used further ensures the formation of a platinum chloride complex that is stable at pH values below 2. This furthermore assists in preventing hydrolysis and the subsequent adsorption of the hydrolysis product on the undissolved substrate[4].

Although *aqua regia* achieves a good PGM yield and provides good PGM stability, it is problematic in its execution. Leaching needs to be conducted at 70-95°C, and at these temperatures the solution becomes extremely unstable and corrosive. Nitric acid is decomposed with subsequent evolution of nitrogen oxides, hydrochloric acid is converted into gaseous hydrogen chloride, and chlorides are oxidised to gaseous chlorine[4,6,24,25]. This severe loss of oxidising agent (nitric acid) and complexing agent (chlorides) makes for a huge consumption of reagents.

It has been found that the dissolution of Pt and Pd are linked to the ratio of HCl:HNO_3[12,20]. Pt dissolution increased for decreasing rations of HCl:HNO_3, whereas Pd dissolution increased for increasing rations of HCl:HNO_3. This observation has been ascribed to the fact that platinum undergoes a redox reaction while in the ionic state, whereas palladium only goes from the metal to the ion[13,20].

Using a packed bed system Bautista et al[12] obtained dissolution yields of 96% for Pd and 73% for Pt with a 3.65M HCl and 0.35M HNO_3 solution. Decreasing the HCl:HNO_3 ratio to 3M:1M resulted in dissolution yields of 76% Pd and 98% Pt. Employing a fluidised bed did not result in as good dissolution yields, and was the best yield (93% Pt and 78% Pd) achieved with substitution of HCl with $HClO_4$, i.e. 3M $HClO_4$:1M HNO_3.

In recovering Pt dust, that is lost from a platinum gauze catalyst during the manufacturing of nitric acid from ammonia, Barakat and Mahmoud[26] employed *aqua regia* and achieved a maximum recovery of 98% after 1.5h at 109°C and a liquid/solid ratio of 10.

Platinum/rhenium bimetallic catalysts are widely used for the production of high octane fuels. Investigating the recovery of Pt from such a spent catalyst, Jafarifar et al[27] employed a straight aqua *regia* leach as well as a microwave assisted *aqua regia* leach. In the case of the straight *aqua regia* leach a maximum dissolution yield of 96.5% was achieved after 2.5h at 109°C and a liquid/solid ratio of 5. In the case of the microwave assisted *aqua regia* leach the dissolution yield increased to 98.3% after only 5 minutes with a liquid/solid ratio of 2.

As part of the Fischer-Tropsch (FT) process to produce hydrocarbons from synthetic gas (syngas), metal catalysts are used that consist of high loads of cobalt and small amounts of platinum on, amongst others, an alumina support. As part of a first stage sodium hydroxide-nitric acid leach, to recover aluminium and cobalt (99.97% and 99.7% dissolution yields respectively), 37.5% platinum was dissolved. In a subsequent *aqua regia* leach at 80°C of the first stage insoluble residue, almost all of the platinum was dissolved leaving less than 0.01%[28].

2.2 $AlCl_3$ / HCl / HNO_3

The above-mentioned problems with *aqua regia* have been overcome by partial replacement of the hydrochloric acid with a non-volatile chloride salt such as aluminium chloride[6,24,25]. $AlCl_3$ is a good complexing agent substitute compared to other common chloride salt, e.g. NaCl, KCl, $MgCl_2$ or $CaCl_2$, as it provides three chloride ions per molecule of aluminium chloride, and it furthermore reduces the rate of substrate dissolution, which could be either γ-alumina or α-alumina[4].

Angelidis and Skouraki[4] investigated the recovery of Pt from a spent industrial catalyst containing only Pt as a precious metal. Instead of *aqua regia* they used aluminum chloride solutions with low concentrations of nitric acid as an oxidant. The effect of aluminum chloride and nitric acid concentrations on the yield of platinum dissolution was studied, and they found that 75-100% substitution of hydrochloric acid by aluminum chloride (2M), with low nitric acid concentration (1M), did not affect the platinum dissolution yield at all. Substitution of hydrochloric acid with aluminum chloride furthermore serves to reduce the volume of released gases by 60%, minimising excess reagent consumption. All experiments were conducted in the temperature range of 103-109°C. No mention was however made as to the effectiveness of the process at lower temperatures.

Although substrate dissolution dropped from 25% to 12% upon substitution of hydrochloric acid with aluminum chloride[24], dissolution of other metals like manganese, lead and iron were observed, which under ideal conditions are not wanted.

A study by Bolinski and Distin[23], investigating the effect of different compositions of the $AlCl_3/HCl/HNO_3$-system on the recovery of Pt and Rh from a spent autocatalyst, at temperatures between 80°C and the boiling point (105-107°C), revealed that a system concentration of 0.29M $AlCl_3$, 1.66M HCl, and 3.5M HNO_3 resulted in the highest yield for both Pt and Rh. It is interesting that in the absence of $AlCl_3$ about 8M HCl is required to obtain the maximum yield of 95% for Pt and 87% for Rh. It was however impossible to raise the $AlCl_3$ content above 0.29M via the addition of $AlCl_3.6H_2O$. The authors ascribe the high reactivity of the $AlCl_3/HCl/HNO_3$-system, relative to the HCl/HNO_3-system, to enhanced chloride ion activity. They have however not calculated the ionic activities, but do mention that methods for estimating activities in mixed chloride solutions at high ionic strengths and high temperatures have been described[29]. The presence of nitric acid though provides difficulties in that it interacts with hydrochloric acid in a complex manner that is difficult to define, forming additional dissolved and gaseous species.

At the lower temperature of 80°C the yield for both Pt and Rh dropped compared to dissolution at boiling point.

In a subsequent study[23] by the above-mentioned authors they set out to improve the yield, mainly by upping the aluminum chloride concentration above 0.29M. For platinum a slight improvement to ±96% was achieved at 0.48M, but no discernable improvement resulted beyond that. In the case of rhodium a marked increase in the yield to ±90% was achieved with 0.8M aluminum chloride. Leaches were also conducted at 120°C, 140°C, and 160°C respectively in an autoclave, and although increased extraction rates were obtained the final recoveries were essentially the same as at the boiling point.

Angelidis[30] has also employed aluminum chloride as part of an oxidation leach, but pre-empted that with a reduction leach. According to the author a reduction leach is required to destabilise the washcoat, which due to the presence of large quantities of CeO_2 (20-30% in the washcoat) is not completely soluble under oxidizing conditions. H_2SO_4 was used as an acidity source and $N_2H_6SO_4$ as a reduction reagent. The oxidation leach solution consisted of HCl (5%) as the acidity source, $AlCl_3$ (0.33M) as the source for chloride ions, and NaOCl (4% initially, with subsequent addition) as a chlorine source in order to produce the required oxidative environment. The best individual yields obtained were 96.6% for Pt and 97.2% for Rh, while the best combined yield achieved was 95.8% for Pt and 95.5% for Rh.

2.3 Fluoride (F^-)

Although fluoride, being a hard base (more so than the other halides), is a strong complexing agent, almost no work has been conducted using fluoride for the processing of spent catalysts containing PGMs. A study conducted by Pinheiro et al[31] revealed that (i) with 20M HF very little Pt (5 wt%) was recovered together with only a little alumina dissolution (9 wt%) as well, (ii) combining 20M HF with 12M HCl resulted in only a slight increase with regard to Pt recovery, i.e. 7 wt%, but basically all (> 99 wt%) of the alumina substrate was dissolved, (iii) substituting HCl with 36 wt% H_2O_2 in the presence of 20M HF, resulted in an increased Pt recovery to 10 wt% with alumina dissolution still greater than 99 wt%, and (iv) combining all three, i.e. 20M HF + 36 wt% H_2O_2 + 12M HCl, further increased Pt recovery to only 15 wt% with alumina dissolution still greater than 99 wt%. This technique would therefore seem to be not effective for PGM dissolution. It is however a very good technique for substrate dissolution, but small amounts of Pt are co-dissolved as well making it problematic. It has been postulated by the authors that H_2O_2 has a physical effect on the solubilisation step of the alumina in that its vigorous decomposition (catalysed by platinum metal) seems to assist grinding of the substrate.

Given the fact that we have seen that the $AlCl_3/HCl/HNO_3$-system is as effective (even more so) as *aqua regia*, with the added benefit of being less aggressive and using less reagents, this obviously begs the question how the $AlF_3/HF/HNO_3$ system would compare? No literature was found related to this topic.

2.4 Cyanide (CN^-)

It has been claimed that the cyanide leaching method is more cost effective and environmentally friendly than conventional melting and acid recovery techniques, while still achieving a 90% dissolution of PGM[32]. However, this technique requires high temperatures and pressures, i.e. 160°C and 75psig for the leach, followed by decomposition of the cyanide at 250-275°C and 2758-6206 kPa producing a PGM powder.

Shams et al[3] investigated the recovery of platinum from a selective linear paraffin dehydrogenation spent catalyst using cyanide leaching. A maximum recovery of 95% was achieved with a 1 wt% NaCN solution at 140°C, pH 8-9, and pressures between 618 and 1002 kPa. It was observed that recovery started to improve below pH 9.5. According to the authors the formation of the cyanoplatinate complex is a chemical oxidation reaction, and as it is well established that the oxidation reduction potential (ORP) is related to the concentration of the hydrogen ion, and therefore the pH of the solution via the Nernst equation, suggesting that at lower pH values the chemical oxidation reaction is further enhanced, resulting in the formation of the more stable tetracyanoplatinate complex, which thermodynamically becomes more favourable.

Studying the recovery of PGM from virgin automotive catalysts by cyanide leaching, Atkinson et al[21] concluded that chemical reduction of the catalyst with H_2 at 550°C for 1h, prior to leaching, was critical for high recoveries. Using a solution of 5% NaCN and 1% promoter, at its natural pH of about 11.8 and 80°C for 1h, dissolved 99% Pd and 98% Pt and Rh. A proprietary promoter was added to enhance the dissolution rate.

A study, subsequent to the above, conducted by Desmond et al[33] on both virgin and used catalyst, showed slightly different results. Leaching was again conducted in an autoclave with a 5% NaCN solution for 1h. For the virgin catalyst best leaching results were obtained at 160°C; at this temperature 97% Pt and Pd and 90% Rh were dissolved. For the used catalyst best results were again obtained at 160°C with recoveries for Pt, Pd, and Rh of 88%, 80%, and 75% respectively. Pretreatment of the used catalyst however did not enhance the extraction of PGMs. There would therefore seem to be a bit of a discrepancy between the two studies (by the very same authors).

The above-mentioned authors (but one) again tried their hands at the cyanide leaching of PGMs. In this instance however they operated a 2kg batch process for the recovery of PGMs from automobile catalysts[34]. About 95% of the PGM was dissolved from the virgin catalyst using a two stage autoclave leach at 160°C for 1h with a 0.1N NaOH and 1% NaCN leach solution. Between 85 and 90% of the PGM was dissolved from the used catalyst by leaching three times in an autoclave at 160°C for 1h with a 0.1N NaOH and 1% NaCN solution.

It would seem that the chemistry of the PGM recovery by high temperature cyanide leaching from spent catalysts is quite complex and still poorly understood. Ultraviolet spectroscopy studies by Sibrel and Atkinson[35] and Sibrel et al[36] have shown that Pt and Pd are solubilised as the square planar tetracyanometallate(II) complex, while Rh is solubilised as the octahedral hexacyanorhodate(III) complex.

2.5 Thiosulphate ($S_2O_3^{2-}$), Thiourea (NH_2CSNH_2), and Thiocyanate (SCN^-)

In considering other potential lixiviants for the leaching of PGMs we will look to gold, as a number of alternatives to cyanide have been researched for the leaching of gold ores and gold concentrates. A number of articles, and review articles, have been published on the leaching of gold (and silver) with thiosulphate as a replacement for the cyanide leaching process. Although a number of alternative lixiviants for leaching of gold ores have been examined, none has made any significant inroad into the dominant position of cyanide as yet[37]. As pointed out above, a few articles have been published on the leaching of PGMs with cyanide, but it would seem that no work has been conducted on the leaching of PGMs with thiosulphate, thiourea, or thiocyanate as no literature could be found on it.

Reviewing the most promising alternative gold leaching agents to cyanide, Hilson and Monhemius[37] conclude that, "in spite of the vociferous opposition to the use of cyanide in the gold mining industry by sections of the environmental movement, unless further research and development makes one or more of the alternative lixiviants economically competitive, it will continue to be the only practical leach reagent in large-scale gold extraction processes." They do however highlight three potential alternative lixiviants that warrant further research and development.

Thiourea (NH_2CSNH_2) has shown considerable promise as a gold extraction agent. The reaction is rapid and gold extractions of up to 99% can be achieved in acidic conditions[37,38], with thiourea forming a cationic complex according to the following anodic reaction:

$$Au + 2CS(NH_2)_2 \rightarrow Au[CS(NH_2)_2]_2^+ + e^- \qquad ...19$$

In acidic and neutral mediums thiourea is thermodynamically fairly stable, but decomposes rapidly in alkaline mediums[37,39]. The use of ferric ions in sulphuric acid would seem to be the most effective system[37,40]. Thiourea is however more expensive than cyanide, its consumption in gold processing is high, and the gold recovery step requires more development[37,41].

Thiocyanate (SCN^-) has proved to be an "effective lixiviant for gold in acidic conditions, yielding dissolution rates that are comparable to those obtained with thiourea whilst offering the advantage of much greater stability against oxidative decomposition." [37,42,43] Recoveries of 95% have been achieved[44]. In the presence of Fe(III) as an oxidising agent, Fe(III) is reduced to Fe(II) while SCN^- is oxidised to several intermediate species including $(SCN)_3^-$ and $(SCN)_2$, which can both oxidise and complex gold[37].

Thiosulphate ($S_2O_3^{2-}$) has been extensively researched as an alternative lixiviant for gold dissolution. In contrast to thiourea and thiocyanate, gold dissolves slowly in alkaline thiosulphate[38], but the rate is markedly enhanced in the presence of ammonia and copper ions[45,46,47]. The activation energy required to dissolve metallic gold in the presence of ammonia (pH 10), excess thiosulphate and Cu(II) is 15.54 kJ/mol. In the absence of ammonia and Cu(II), however, the activation energy rises to 27.99 kJ/mol, demonstrating the catalytic effects of ammonia and Cu(II)[48]. Gold forms a stable anionic complex with thiosulphate according to the following reaction:

$$4Au + O_2 + 8S_2O_3^{2-} + 2H_2O \rightarrow 4[Au(S_2O_3^{2-})_2]^{3-} + 4OH^- \qquad ...20$$

The above is actually the net reaction of the following[48]:

$$Au + [Cu(NH_3)_4]^{2+} + 3S_2O_3^{2-} \rightarrow [Au(NH_3)_2]^+ + [Cu(S_2O_3)_3]^{5-} + 2NH_3 \qquad ...21$$

$$[Au(NH_3)_2]^+ + 2S_2O_3^{2-} \rightarrow 4[Au(S_2O_3^{2-})_2]^{3-} + 2NH_3 \qquad ...22$$

$$4[Cu(S_2O_3)_3]^{5-} + 16NH_3 + O_2 + 2H_2O \rightarrow 4[Cu(NH_3)_4]^{2+} + 12S_2O_3^{2-} + 4OH^- \qquad ...23$$

Thiosulphate is metastable, resulting in it being readily oxidised or reduced according to the initial solution potential. Thiosulphate can break down into sulfite, sulfate, trithionate, tetrathionate, sulphide, poythionates ($S_xO_y^{2-}$) and/or polysulfides (S_x^{2-}), depending on the aqueous environment. The pH of the solution is also important and are alkaline conditions required, as it is readily decomposed in acidic medium. Certain metal ions and reagents also cause the breakdown of thiosulphate according to the following reactions[48]:

$$4S_2O_3^{2-} + 4H^+ + O_2 \rightarrow 2S_4O_6^{2-} + 2H_2O \qquad ...24$$

$$S_2O_3^{2-} + 4H^+ \rightarrow S^0_{(ppt)} + SO_{2\,(g)} + H_2O \qquad ...25$$

$$4S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 2S_4O_6^{2-} + 4OH^- \qquad ...26$$

$$S_2O_3^{2-} + CN^- + ½O_2 \rightarrow SCN^- + SO_4^{2-} \qquad ...27$$

$2[Fe(S_2O_3)]^{+} \rightarrow 2Fe^{2+} + S_4O_6^{2-}$ ...28

$S_2O_3^{2-} + Cu^{2+} + 2OH^{-} \rightarrow SO_4^{2-} + H_2O + CuS_{(ppt)}$ ...29

$2Cu^{2+} + 2S_2O_3^{2-} \rightarrow 2Cu^{+} + S_4O_6^{2-}$ ...30

The anions trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$), however, are not known to have any lixiviant activity[46]. There are, however, also many reactions whereby thiosulphate is generated, contributing to the leach.

Some PGM thiosulphate complexes are known, but their stability constants are unknown[49]. $[Pd(S_2O_3)_4]^{6-}$ and $[Pt(S_2O_3)_4]^{6-}$ do have aqueous solubilities above 10 ppb at pH 7 and 25°C, and low oxidation potentials (- E°) of 0.116 0.170 mV respectively[50,51]. These complexes, however, are thermodynamically unstable, and slowly decompose into insoluble S-bridged oligomers[52].

Investigating the leaching of a Turkish gold ore with cyanide, thiourea and thiosulphate, Tanriverdi et al[53] found that all processes gave recoveries in excess of 90%, with thiosulphate the highest at 96%, over a 48h period. Both thiourea and thiosulphate consumption however were found to be excessively high.

2.6 Summary

- ✓ Aqua Regia (HCl/HNO_3) as a lixiviant resulted in individual dissolution yields of 98% for Pt and 96% for Pd respectively, but suffers from severe loss of oxidising agent (nitric acid) and complexing agent (chlorides) resulting in huge consumption of reagents.
- ✓ For the $AlCl_3/HCl/HNO_3$ system individual dissolution yields of 96.6% for Pt and 97.2% for Rh were achieved, which is comparable to that of aqua regia, but the great benefit of this system is that it reduces the volume of released gasses by 60%.
- ✓ Fluoride (F^-) seems to be not effective for PGM dissolution, but for substrate dissolution it would seem to be very effective. However, as small amounts of Pt are co-dissolved with the substrate it becomes problematic.
- ✓ Cyanide (CN^-) does result in good dissolution yields, e.g. 98% Pt and 99% Pd, but requires high temperatures and pressures.
- ✓ Thiosulphate ($S_2O_3^{2-}$), thiourea (NH_2CSNH_2), and thiocyanate (SCN^-) have shown great promise with regard to the dissolution of gold, i.e. 96%, 99% and 95% respectively, but as yet have not been tested for PGM dissolution.

Chapter 3

THERMODYNAMICS

3.1 Introduction

Based on the literature review conducted, the potential of leaching Pt^0, Pd^0 and Rh^0 with thiosulphate ($S_2O_3^{2-}$), thiourea (NH_2CSNH_2), and thiocyanate (SCN^-) will be investigated electrochemically. These ligands show good results for the leaching of gold, but have not been tested as yet for the PGMs. This will be compared to the electrochemical investigation of the leaching of Pt^0, Pd^0 and Rh^0 with $AlCl_3/HCl/HNO_3$ as this system shows great promise in comparison with aqua regia with the added benefit of using less oxidant and ligand (by as much as 60%).

Before the electrochemistry is to be investigated though, a thermodynamic study is to be conducted. This will shed light on the stability of the different PGM-complexes in respect of the applied potential (E_h) and the prevailing pH, i.e. E_h pH diagrams, also known as Pourbaix diagrams will be constructed. These diagrams, however, only depict the stability regions for specific complexes, and do not convey any information about the kinetics of the leaching process, which can only be obtained from experimental data.

3.2 Experimental

HSC Chemistry 6, a software package developed by Outokumpu, was used for the preparation of E_h pH diagrams. To be able to construct an Eh pH diagram that contains a specific species, the formation constant (stability constant) of that specific species needs to be known. From this formation constant the free energy of formation, i.e. ΔG_f, can be calculated, leading to the standard enthaply of formation ($H_f°$), which is required by HSC to develop the different stability regions.

Although HSC has its own database containing thermodynamic data of different aqueous, gaseous and solid species, both the IUPAC Database of Stability Constants and the NIST Database for Critically Selected Stability Constants have been employed to search for available stability constants of complexes of Pt, Pd and Rh with $S_2O_3^{2-}$, NH_2CSNH_2, SCN^- and Cl^-, as well as OH^-, as HSC's database is by no means complete, especially for the PGMs. E_h pH diagrams are only as good as (a) the available data and (b) the availability of data. A lot more data is available on the complexation of PGMs with chloride and hydroxide compared to $S_2O_3^{2-}$, NH_2CSNH_2, and SCN^-. To that regard the E_h pH diagrams of the different PGMs with $S_2O_3^{2-}$, NH_2CSNH_2, and SCN^- are not necessarily as realistic as those of chloride. The following tables contain the available stability constants apart from those species already contained as part of HSC's database.

Ligand	**Element**			**Formula**	**log β**	**Reference**
	Pt	**Pd**	**Rh**			
Cl^-	Pt^{2+}			$[ML]/[M].[L]$	5.00	58
	Pt^{2+}			$[ML_2]/[M].[L]^2$	9.00	
	Pt^{2+}			$[ML_3]/[M].[L]^3$	11.80	
	Pt^{2+}			$[ML_4]/[M].[L]^4$	13.80	
		Pd^{2+}		$[ML]/[M].[L]$	4.47	59
		Pd^{2+}		$[ML_2]/[M].[L]^2$	7.74	
		Pd^{2+}		$[ML_3]/[M].[L]^3$	10.20	
		Pd^{2+}		$[ML_4]/[M].[L]^4$	11.50	
			Rh^{3+}	$[ML]/[M].[L]$	2.49	60
			Rh^{3+}	$[ML_2]/[M].[L]^2$	4.45	
			Rh^{3+}	$[ML_3]/[M].[L]^3$	6.14	
			Rh^{3+}	$[ML_4]/[M].[L]^4$	7.61	
			Rh^{3+}	$[ML_5]/[M].[L]^5$	8.11	
			Rh^{3+}	$[ML_6]/[M].[L]^6$	7.82	
$S_2O_3^{2-}$	Pt^{2+}			$[ML_4]/[M].[L]^4$	43.70	61
		Pd^{2+}		$[ML_4]/[M].[L]^4$	35.00	
NH_2CSNH_2	Pt^{2+}			$[ML_4]/[M].[L]^4$	38.60	
		Pd^{2+}		$[ML_4]/[M].[L]^4$	30.30	
SCN^-	Pt^{2+}			$[ML_4]/[M].[L]^4$	33.60	62
		Pd^{2+}		$[ML_4]/[M].[L]^4$	26.80	
OH^-		Pd^{2+}		$[ML]/[M].[L]$	11.72	63
		Pd^{2+}		$[ML_2]/[M].[L]^2$	23.57	
		Pd^{2+}		$[ML_3]/[M].[L]^3$	25.42	
		Pd^{2+}		$[ML_4]/[M].[L]^4$	26.42	
		Pd^{2+}		$[M][L]^2/[ML_2(s)]$	-28.5	
			Rh^{3+}	$[ML]/[M].[L]$	11.03	64
			Rh^{3+}	$[ML_2]/[M].[L]^2$	21.47	
			Rh^{3+}	$[ML_3]/[M].[L]^3$	31.52	
			Rh^{3+}	$[ML_4]/[M].[L]^4$	38.29	
			Rh^{3+}	$[ML_5]/[M].[L]^5$	43.06	
			Rh^{3+}	$[ML_6]/[M].[L]^6$	46.36	

Table 1 Stability constants for Pt, Pd and Rh with ligands of interest.

Ligand	**Complex**		**Formula**	**log β**	**Reference**
	Pd	**Rh**			
OH^-	$PdCl_4^{2-}$		$[ML'_3L].[L']/[ML'_4].[L]$	16.48	59
	$PdCl_4^{2-}$		$[ML'_2L_2].[L']^2/[ML'_4].[L]^2$	20.63	
	$PdCl_4^{2-}$		$[ML'L_3].[L']^3/[ML'_4].[L]^3$	24.02	
	$PdCl_4^{2-}$		$[ML_4].[L']^4/[ML'_4].[L]^4$	26.23	
		$RhCl_4^-$	$[ML'_4L_2]/[ML'_4].[L]^2$	25.64	65
		$RhCl_4^-$	$[ML'_3L_3].[L']/[ML'_4].[L]^3$	34.46	

Table 2 Stability constants for Pt, Pd and Rh with mixed chlorides and hydroxides.

For each cation and anion involved in complexation, the standard enthalpy and entropy values are as follows. These values have been obtained from HSC 6 and the CRC Handbook of Chemistry and Physics (70th Edition).

Ion	$H_f°$, kJ/mol	$S_f°$, kJ/(mol.K)	Reference
Pt^{2+}	243.55	-9.0000E-02	66
Pd^{2+}	176.06	-9.4560E-02	
Rh^{3+}	179.20	-2.9957E-01	
Cl^-	-167.08	5.6735E-02	
OH^-	-230.02	-2.0240E-02	
SCN^-	76.44	1.4435E-01	
$S_2O_3^{2-}$	-648.52	6.6944E-02	
H_2NCSNH_2	-88.28	Not Available	57

Table 3 Thermodynamic data for the individual cations and anions.

The Gibbs free energy of formation for each complex can be calculated using the following formula:

$\Delta G° = - R.T\ 2.303 \log \beta$, where R = 8.314 J/(K.mol) and T = 298.15 K.

For example, for $PtCl_4^{2-}$ (Table 1)

$$\begin{aligned} \Delta G° &= - R.T\ 2.303 \log \beta \\ &= - 8.314\ \mathrm{J/(K.mol)}.(298.15\ \mathrm{K}).(2.303).14 \\ &= - 79.92\ \mathrm{kJ/mol} \end{aligned}$$

Therefore, if we consider the formation of $PtCl_4^{2-}$ from its elements, the standard Gibbs free energy of formation for $PtCl_4^{2-}$ can be calculated:

$Pt^{2+} + 4Cl^- \rightarrow PtCl_4^{2-}$

$$\begin{aligned} \Rightarrow \quad \Delta G° &= -79.92\ \mathrm{kJ/mol} = G°[PtCl_4^{2-}] - G°[Pt^{2+}] - 4.G°[Cl^-] \\ \therefore\ G°[PtCl_4^{2-}] &= \Delta G° + G°[Pt^{2+}] + 4.G°[Cl^-] \\ &= \Delta G° + H°[Pt^{2+}] - T.S°[Pt^{2+}] + 4.H°[Cl^-] - 4.T.S°[Cl^-] \\ &= -79.92 + 243.55 - 298.15.(-9.0E\text{-}02) + 4.(-167.08) - 4.(298.15).(5.6735E\text{-}02) \\ &= -545.52\ \mathrm{kJ/mol} \end{aligned}$$

The database of HSC require enthalpy (H) and entropy (S) values for each complex. If no entropy data is available we assume a value of zero for the entropy. The subsequent calculated G° value is then used as the enthalpy value.

Furthermore, for $[PdCl_3OH]^{2-}$ (Table 2)

$PdCl_4^{2-} + OH^- \rightarrow [PdCl_3OH]^{2-} + Cl^-$

$$\begin{aligned}\Delta G° &= - R.T\ 2.303 \log \beta \\ &= - 8.314\ J/(K.mol).(298.15\ K).(2.303).(16.48) \\ &= - 94.08\ kJ/mol\end{aligned}$$

$$\Rightarrow \quad G°[PdCl_3OH^{2-}] = H°[PdCl_3OH^{2-}] = -732.51\ kJ/mol$$

And, for $[RhCl_4(OH)_2]^{3-}$ (Table 2)

$RhCl_4^- + 2OH^- \rightarrow RhCl_4(OH)_2^{3-}$

$$\begin{aligned}\Delta G° &= - R.T\ 2.303 \log \beta \\ &= - 8.314\ J/(K.mol).(298.15\ K).(2.303).(25.64) \\ &= - 146.37\ kJ/mol\end{aligned}$$

$$\Rightarrow \quad G°[RhCl_4(OH)_2^{3-}] = H°[RhCl_4(OH)_2^{3-}] = -1105.25\ kJ/mol$$

3.3 Results & Discussion

It has to be noted that all of the Pourbaix Diagrams have been constructed using a metal concentration of 1 mmol/kg H_2O. Employing lower metal concentrations, e.g. 10^{-2} or 10^{-3} mmol/kg H_2O, regions showing solid species could disappear and make way for aqueous species.

3.3.1 Chloride (Cl^-)

From figure 6 it is clear that platinum, in the IV oxidation state, is stable in solution as the hexa-chloride complex below pH 4 and above an E_h value of 0.75V. Above pH 4 oxides of platinum in the II and IV oxidation states are stable. To leach Pt^0 and keep it in stable in solution, the leach has to be conducted at pH-values below 4 and at sufficiently high chloride concentration. For figure 6 the [Cl$^-$] is 1 mmol/kg H_2O.

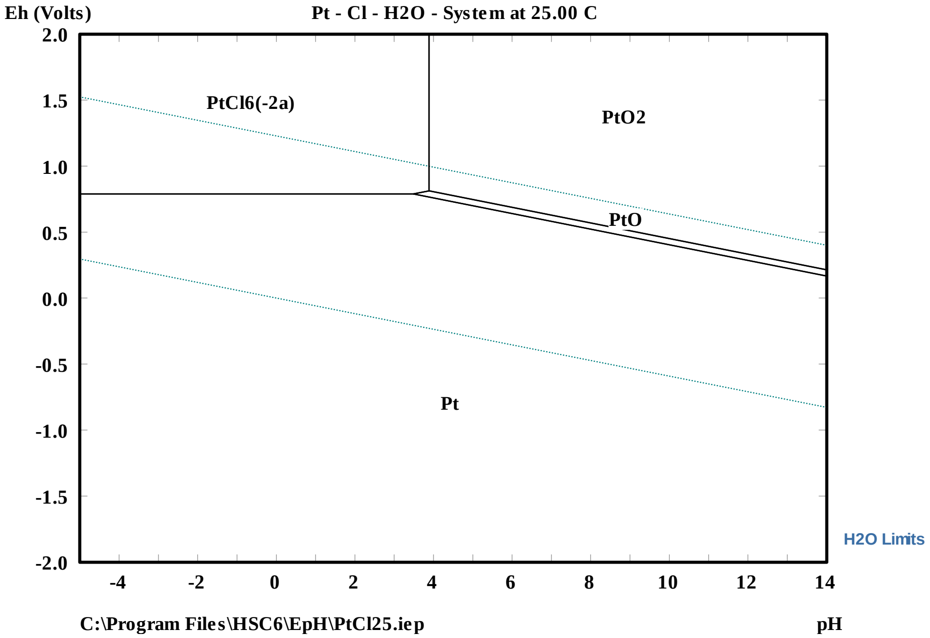


Fig 6 E_h pH diagram for the Pt - Cl - H_2O system, depicting the stability region for the $PtCl_6^{2-}$ complex ([Cl$^-$] = 1 mmol/kg H_2O).

Increasing the chloride-concentration to 10^3 mmol/kg H_2O has a dramatic effect on the chloride stability region for platinum. Platinum(II) is now stable over a very narrow potential-range (≈ 0.5V), above which Pt(VI) is stable. It is clear that the minimum potential for chloride stability has decreased from 0.75V to 0.5V. What is however more evident is that the upper pH limit for chloride stability has increased from < 4 to < 8 (figure 7).

No formation constants for mixed chloride and hydroxide complexes of Pt are known (see figures 8 & 9 for Pd and figures 10 & 11 for Rh), which could have altered the E_h pH diagram.

Palladium on the other hand shows stability regions for the chloride complexes at pH < -2, for the II oxidation state, and pH < 5, for the IV oxidation state at a chloride-concentration of 1 mmol/kg H_2O (figure 8). As data is available for the formation of mixed chloride hydroxide complexes of palladium(II), the stepwise substitution of Cl$^-$ ions with OH$^-$ ions is clearly evident. Increasing the chloride-concentration to 10^3 mmol/kg H_2O again moves the upper pH-limit of the chloride stability regions to higher pH-values, i.e. from pH < -2 to pH < 1 for $PdCl_4^{2-}$, and from pH < 5 to pH < 9.2 for $PdCl_6^{2-}$ (figure 9).

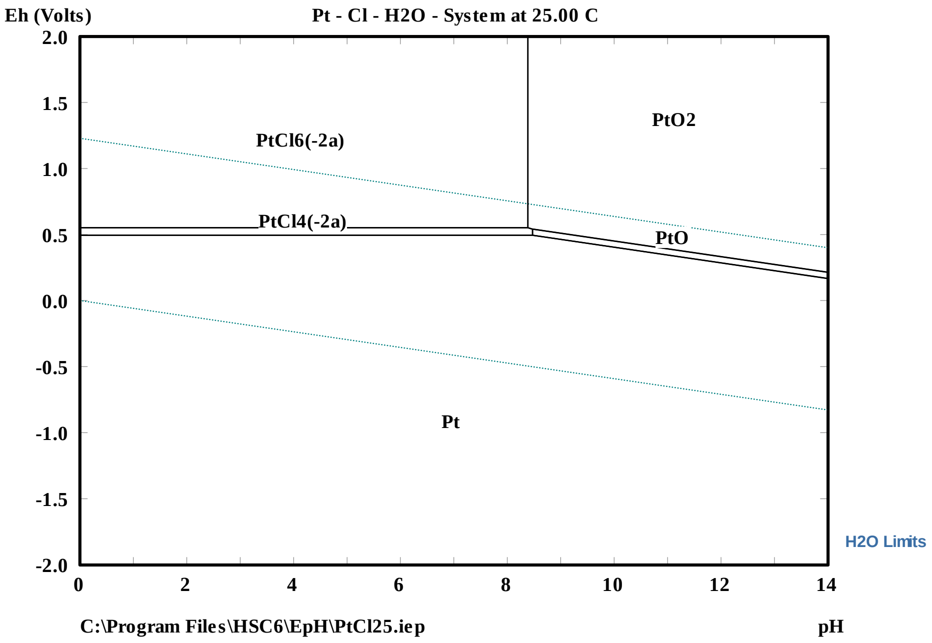


Fig 7 E_h pH diagram for the Pt - Cl - H_2O system, depicting the stability region for the $PtCl_6^{2-}$ complex ([Cl^-] = 10^3 mmol/kg H_2O).

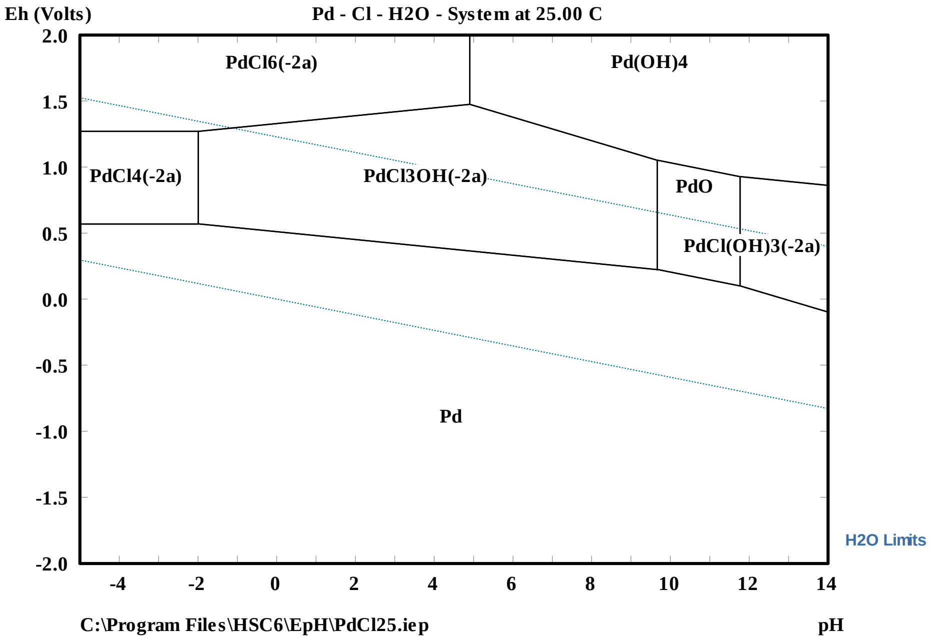


Fig 8 E_h pH diagram for the Pd - Cl - H_2O system, depicting the stability regions for the Pd(II)Cl_4^{2-}-, and Pd(IV)Cl_6^{2-}-complexes ([Cl^-] = 1 mmol/kg H_20).

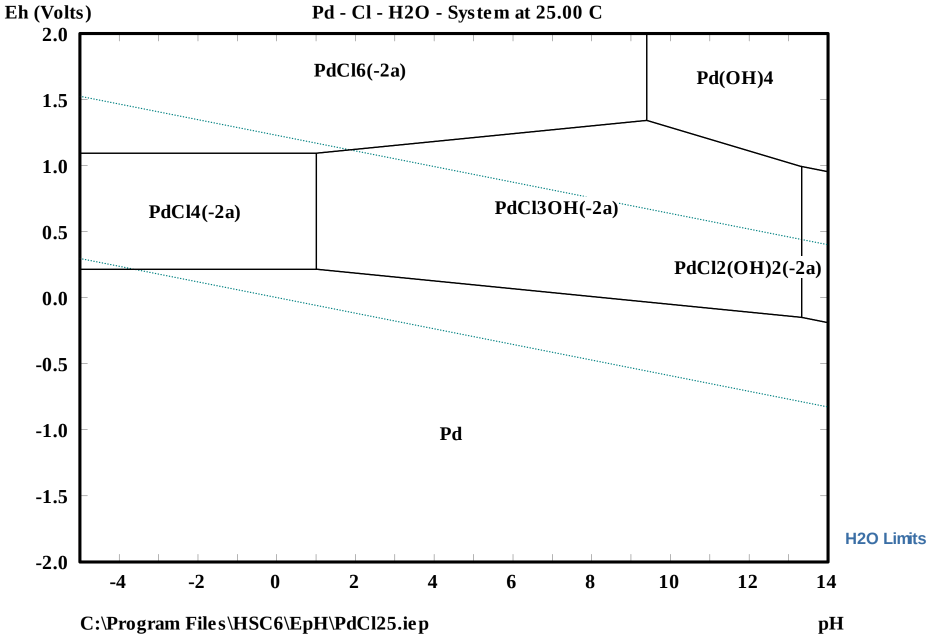


Fig 9 E_h pH diagram for the Pd - Cl - H_2O system, depicting the stability regions for the Pd(II)Cl_4^{2-}-, and Pd(IV)$Cl_6^{2—}$complexes ($[Cl^-] = 10^3$ mmol/kg H_20).

In respect of Rh the $RhCl_5^{2-}$-complex is stable below pH 2 followed by $RhCl_4(OH)_2^{3-}$ between pH 2 and 4. Between pH 4 and 13.7 is a region of insolubility (Rh_2O_3), which could disappear at lower metal concentrations. At a chloride concentration of 1 mmol/kg H_2O, $RhCl_5^{2-}$ is only stable at pH-values less than 2. This increases to 5 for $RhCl_6^{3-}$, at a chloride concentration of 10^3 mmol/kg H_2O, followed by aqueous mixed chloride and hydroxide complexes, highlighting the fact that the region of insolubility has disappeared.

3.3.2 Thiosulphate ($S_2O_3^{2-}$)

With regard to the ‘other’ ligands, i.e. thiosulphate ($S_2O_3^{2-}$), thiourea (H_2NCSNH_2), and thiocyanate (SCN^-), speciation data in respect of the PGMs is extremely limited. E_h pH diagrams are therefore not complete by any means and subsequently do not provide a true picture of what can be expected upon a leach employing one of these ligands.

The stability region for $Pt(S_2O_3)_4^{6-}$, the only aqueous complex (as depicted in figure 12), is across the pH range and above 0V.

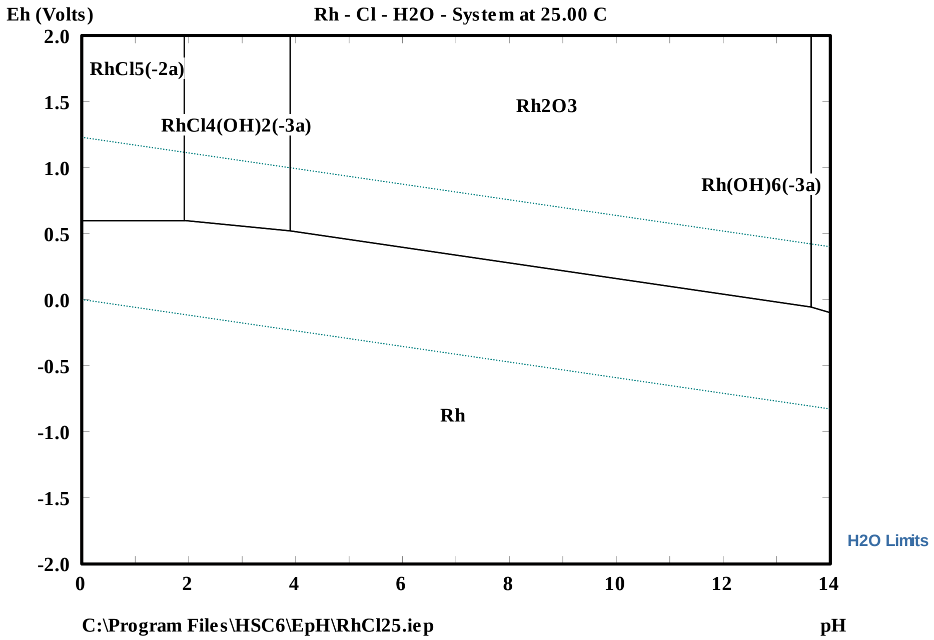


Fig 10 E_h pH diagram for the Rh - Cl - H_2O system, depicting the stability regions for the $RhCl_6^{3-}$- and $RhCl_3(OH)_3^{3-}$-complexes ([Cl^-] = 1 mmol/kg H_20).

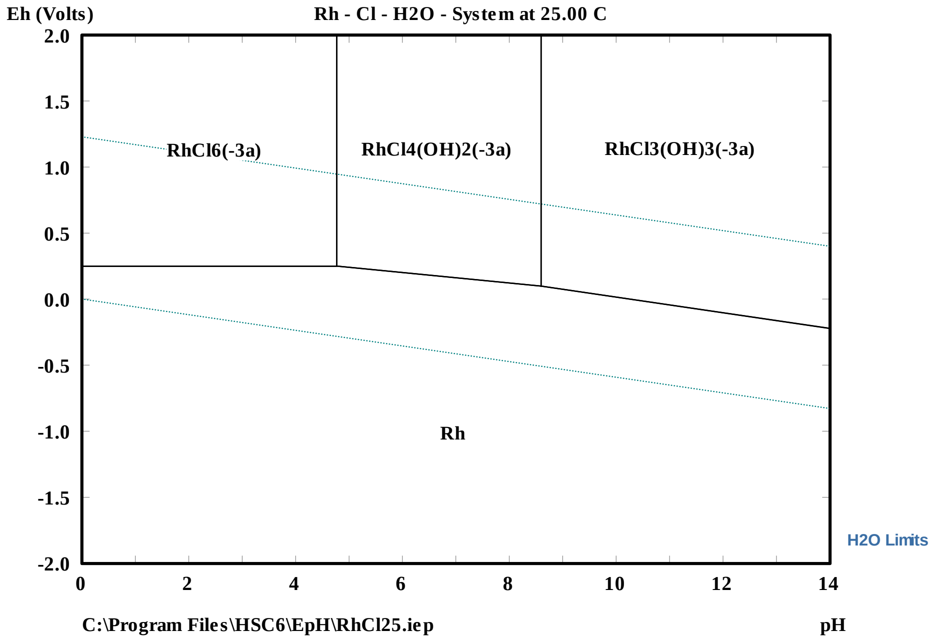


Fig 11 E_h pH diagram for the Rh - Cl - H_2O system, depicting the stability regions for the $RhCl_6^{3-}$- and $RhCl_3(OH)_3^{3-}$-complexes ([Cl^-] = 10^3 mmol/kg H_20).

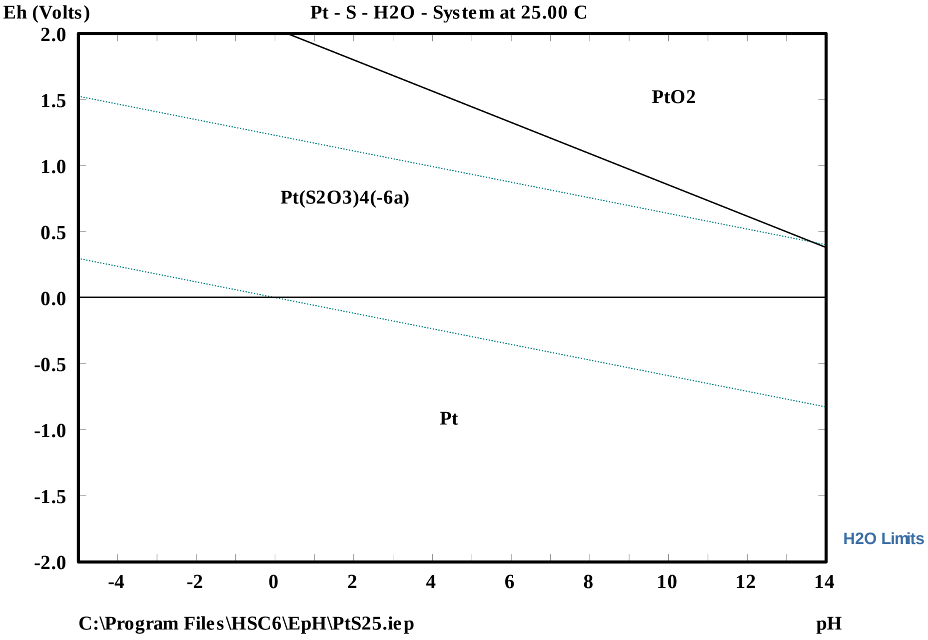


Fig 12 E_h pH diagram for the Pt - S - H_2O system, depicting the stability region for the $Pt(S_2O_3)_4^{6-}$-complex.

For $Pd(S_2O_3)_4^{6-}$, however, the stability region is still across the pH range, but it would seem to be a bit wider in respect of the potential range (figure 13).

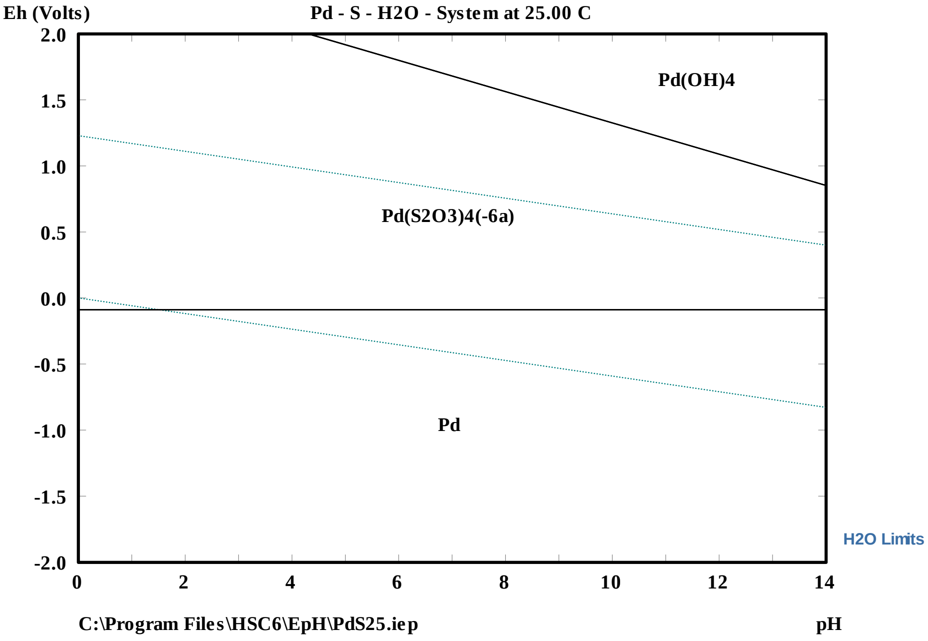


Fig 13 E_h pH diagram for the Pd - S - H_2O system, depicting the stability region for the $Pd(S_2O_3)_4^{6-}$-complex.

3.3.3 Thiourea (NH_2CSNH_2)

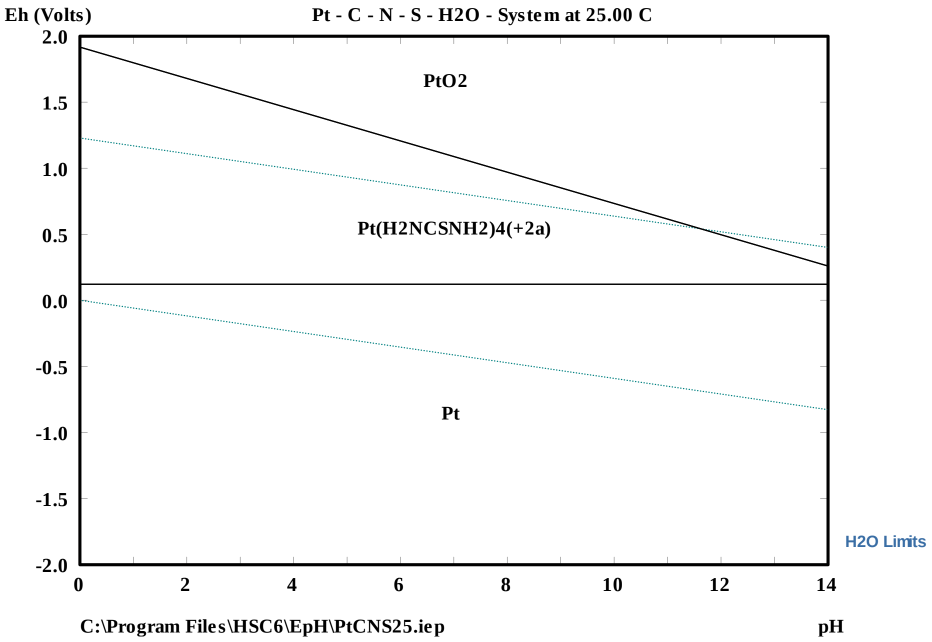


Fig 14 E_h pH diagram for the Pt - C - N - S - H_2O system, depicting the stability region for the $Pt(NH_2CSNH_2)_4^{2+}$-complex.

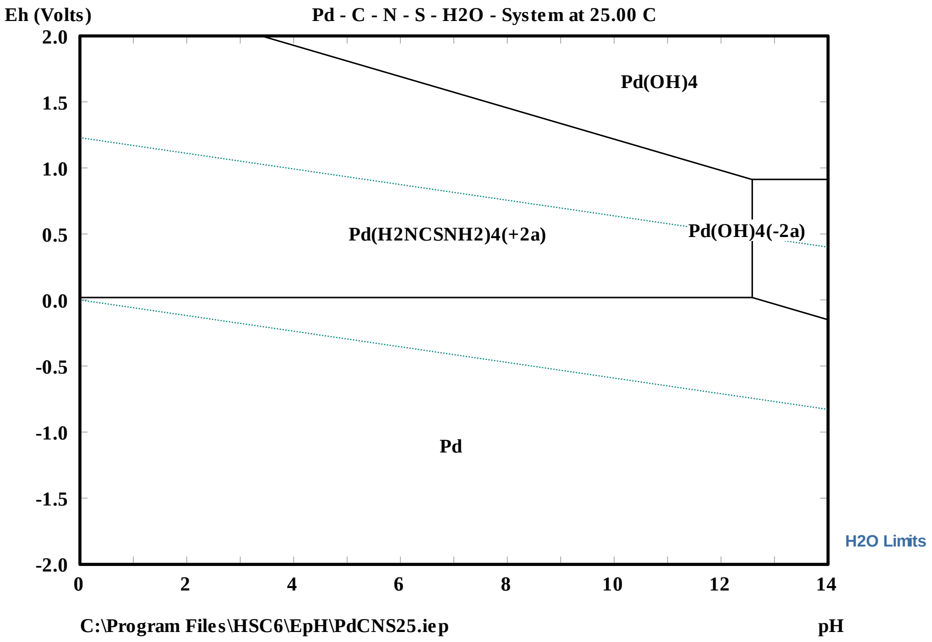


Fig 15 E_h pH diagram for the Pd - C - N - S - H_2O system, depicting the stability region for the $Pd(NH_2CSNH_2)_4^{2+}$-complex.

3.3.4 Thiocyanate (SCN^-)

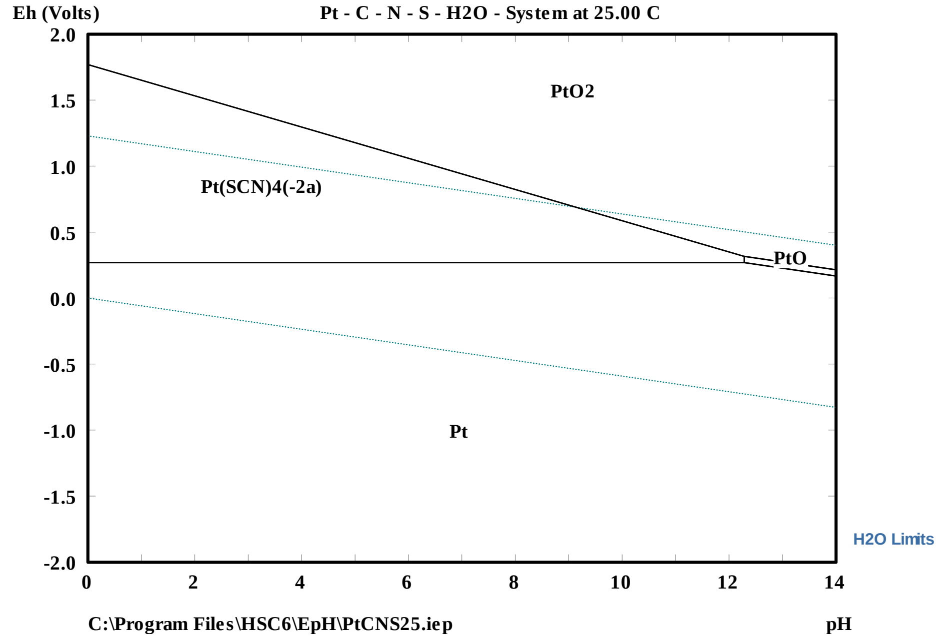


Fig 16 E_h pH diagram for the Pt - C - N - S - H_2O system, depicting the stability region for the $Pt(SCN)_4^{2-}$-complex.

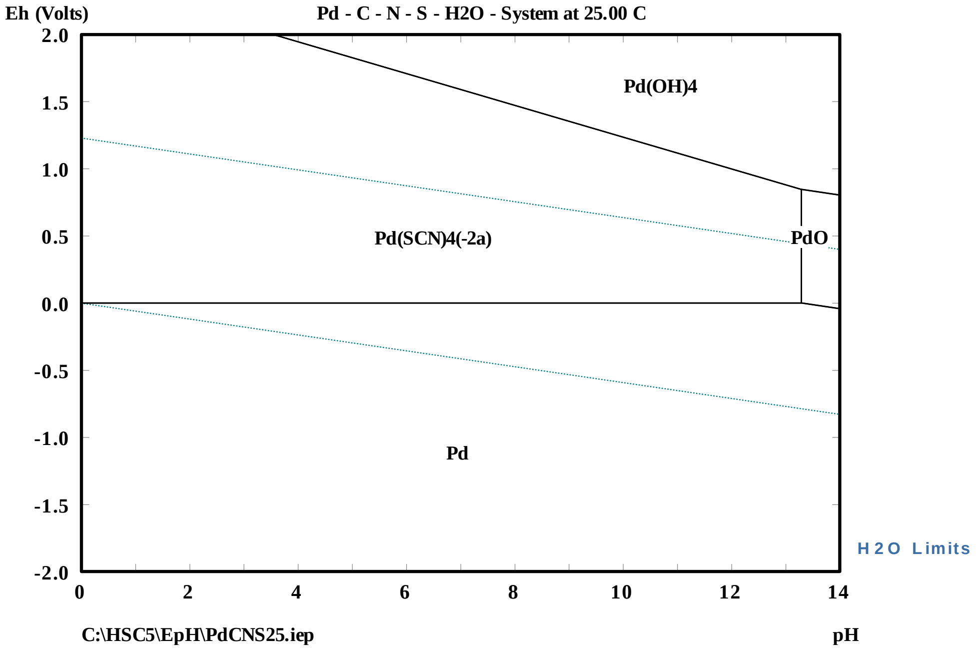


Fig 17 E_h pH diagram for the Pd - C - N - S - H_2O system, depicting the stability region for the $Pd(SCN)_4^{2-}$-complex.

3.4 Summary

All of the ligands show good stability regions with Pt, Pd and Rh, but as mentioned earlier, these diagrams convey no information regarding the kinetics of conversion from the metallic species to an aqueous species. A lot more data is however required on the complexation of Pt, Pd and Rh with $S_2O_3^{2-}$, NH_2CSNH_2, and SCN^-, in order to portray a more realistic or true picture of the different stability regions. This lack of data is especially evident in the fact that no data for the complexation of Rh with $S_2O_3^{2-}$, NH_2CSNH_2, or SCN^- could be obtained. The E_h pH diagrams for these systems could therefore not be reported.

Chapter 4

ELECTROCHEMISTRY

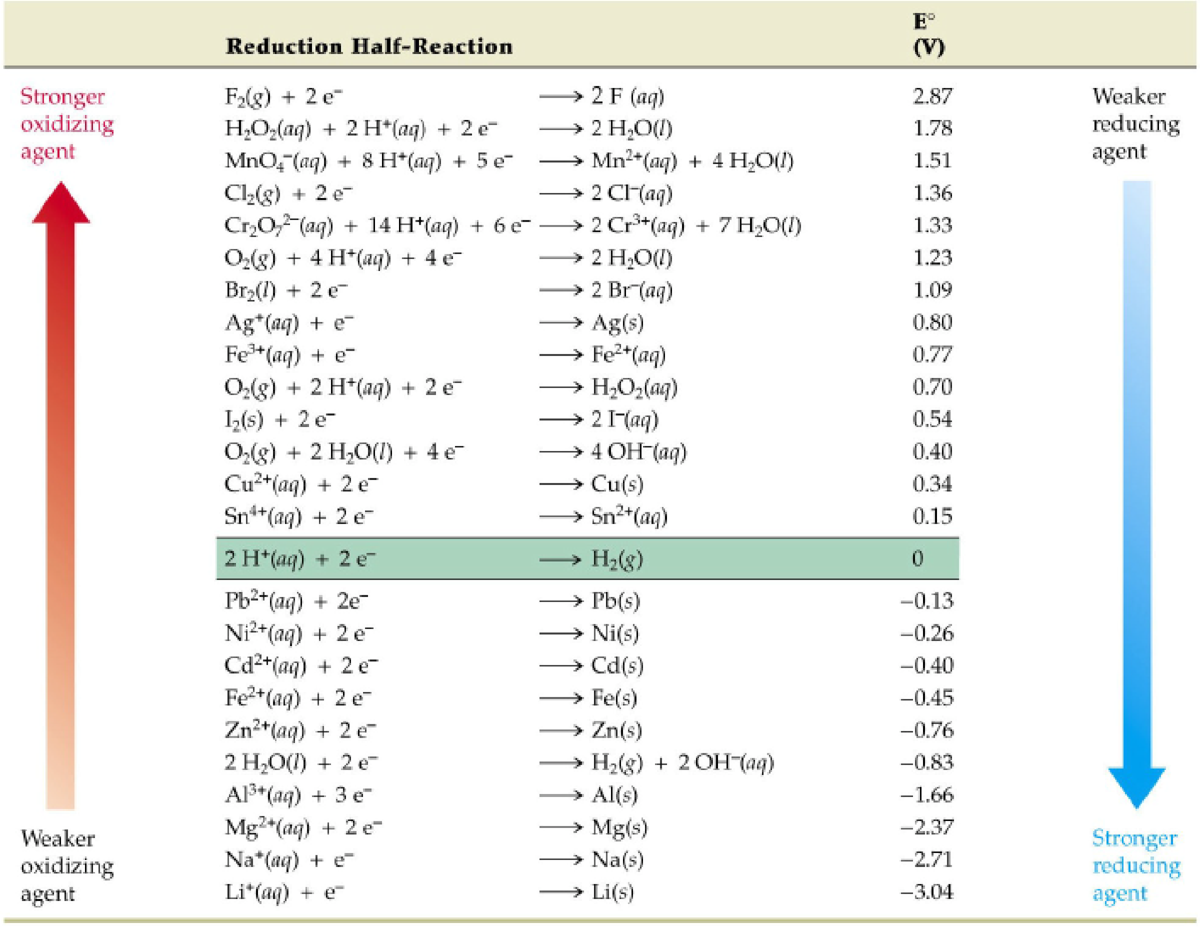
4.1 Introduction

Each species in solution, be it dissolved species, neutral species or solid species (in this case platinum, palladium, and rhodium metal), has its own characteristic current-potential curve. On the resultant curve a potential value (E value) will be found where the sum of the cathodic currents equal the sum of the anodic currents, i.e. equal current flowing in opposite directions[54]. At this point, i.e. at zero net current, in the absence of electrochemical control circuitry the potential corresponds to the metal-solution potential and is called the corrosion potential, E_c[55]. This is also called the open circuit potential, rest potential, or mixed potential.

The rest potential gives an indication as to the potential degree of dissolution/oxidation of a specific PGM by a specific lixiviant relative to other lixiviants. This, however, does not convey anything about the kinetics of dissolution. The potentio-dynamic scan, i.e. current-flow versus potential, conveys the kinetics of the dissolution process as it measures the current-flow per unit area (e.g. $A.cm^{-2}$) at a specific applied potential (V).

Rest potential data were obtained for platinum and palladium with respect to different 'complexing agent / oxidant' systems, i.e. SCN^-/oxidant, $S_2O_3^{2-}$/oxidant, NH_2CSNH_2/oxidant, and $AlCl_3$/HCl/oxidant. The electrochemistry of Rh^0 with different lixiviants was not investigated as we did not have access to a Rh rotating disk working electrode. The cost of acquiring such and electrode was also excessive. Currently no literature is available on the electrochemistry of the interaction between these 'complexing agent / oxidant' systems and any of the PGMs.

According to the table for standard reduction potentials (table 1), the more positive the potential for the reduction half-cell reaction, the more strongly the oxidised species acts as an oxidizing agent. Therefore, for the different oxidizing agents, or lixiviants, the more positive the rest potential, the better oxidizing agent it would be.



	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F\,(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

Table 4 Some standard reduction potentials at 25˚C.

4.2 Experimental

Electrochemical studies have been conducted at Murdoch University (Perth, Australia) on a Princeton Applied Research (PAR) 273 Potentiostat, equipped with a rotating disc working electrode (manufactured with the specific metal to be investigated, i.e. Pt and Pd), employing SoftCorr III software. The rotation speed of the working electrode was 500 rpm in all instances. The rest potential (mixed potential) of the PGM-lixiviant system was determined and a potentio-dynamic scan was conducted across a predetermined potential range.

All electrochemical investigations were conducted in a water jacketed cell at a fixed temperature of 50°C, with the temperature regulated by means of a water bath.

The electrochemical cell consisted of a working electrode, a reference electrode and a counter electrode. In the case of the palladium working electrode, the metal disk had a diameter of 1.0 mm, which translates into an area of 0.00785 cm^2, whilst the metallic section of the platinum electrode had a diameter of 2.013 mm translating into an area of 0.0318 cm^2. The reference electrode used was either a saturated Calomel electrode, i.e. Hg/HgCl, with a potential of 241 mV relative to the hydrogen electrode, or a Hg/HgSO$_4$ electrode with a potential of 650 mV relative to the hydrogen electrode. All measured potentials were re-calculated relative to the standard hydrogen electrode (SHE), and are reported as such.

In those instances where O$_2$ had to be removed, the solution was purged with N$_2$ for 30 minutes and the N$_2$ turned to blanket just prior to the first run.

Stock solutions of the different complexing agents were prepared using the following salts, i.e. NaSCN, Na$_2$S$_2$O$_3$.5H$_2$O, H$_2$NCSNH$_2$, AlCl$_3$.6H$_2$O. Hydrochloric acid (32%), with a SG of 1.19, was used to make up solutions 5% and 10% relative to HCl. In those instances where ferric was employed as oxidant, stock solutions were prepared using Fe$_2$(SO$_4$)$_3$.6H$_2$O.

4.3 Results & Discussion

4.3.1 Thiocyanate (SCN$^-$) / Oxidant

Rest potential scans of Pt^0 and Pd^0 with 0.5 M SCN$^-$ with and without O$_2$ as oxidant, i.e. with and without N$_2$ purging, are depicted in figure 18. We expected the rest potentials in the absence of N$_2$, i.e. with O$_2$ as oxidant, to be higher than the rest potentials in the presence of N$_2$, i.e. in the absence of O$_2$ as oxidant, which is clearly not the case.

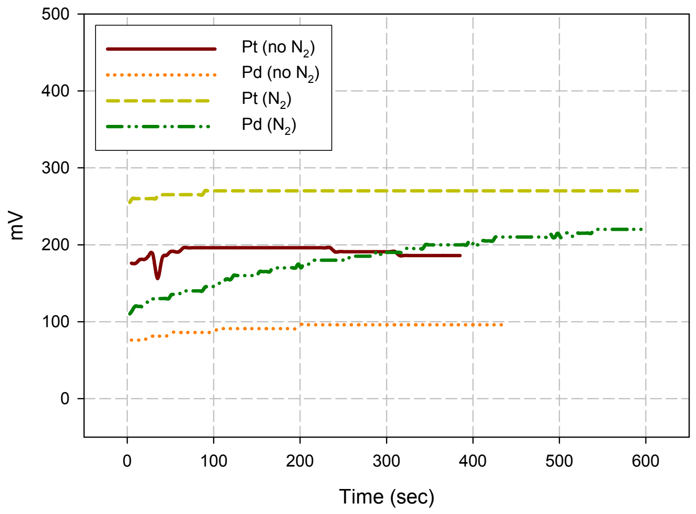


Fig 18 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.5 M SCN$^-$ (with and without N$_2$ purging).**

From figure 18, however, it is clear that the rest potentials for Pt^0 are in both instances (with and without N_2) greater than that for Pd^0. This indicates that the oxidation/dissolution/leaching of Pt^0, in the presence of SCN^-, should progress more easily than Pd^0.

With regard to the kinetics of dissolution of Pt^0 and Pd^0 in the presence of 0.5 M SCN^-, the potentiodynamic scans depicted in figure 19 show that, in the presence of O_2 as an oxidant, the dissolution of Pt^0 is slower than Pd^0. In the absence of O_2, however, the dissolution of Pd^0 is initially slower, but then increases above that of Pt^0 at higher potentials. It is also clear that a non-polished metal surface, in this case Pt^0, leads to an increased rate of dissolution. This is probably due to a greater surface area.

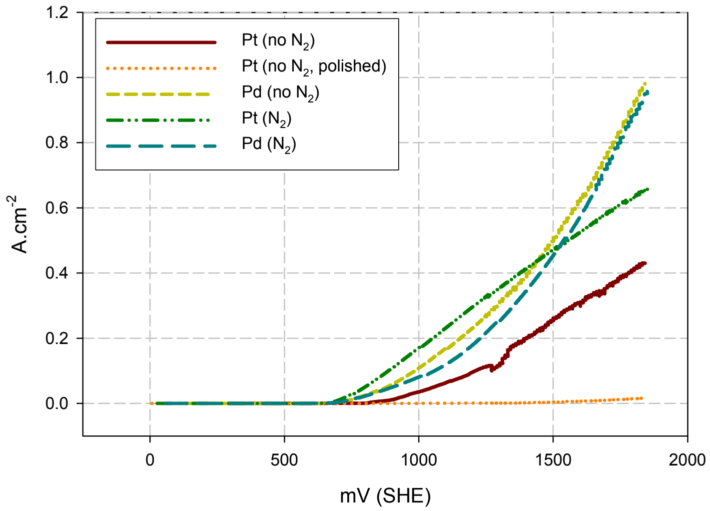


Fig 19 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.5 M SCN^- (with and without N_2 purging).**

Rest potential scans were also obtained for Pt^0 and Pd^0 in the presence of 0.5 M SCN^- at a pH of 2 (figure 20). Again the rest potentials for Pt^0 are greater than that for Pd^0. Scans were repeated for each of Pt and Pd, at the same conditions, and although a clear difference is noticeable between the repeats, there is a clear tendency with regard to the rest potential scans for Pt^0 and Pd^0, in that the rest potentials for Pt^0 are greater than that of Pd^0. In all instances the working electrode was polished prior to the scan being taken.

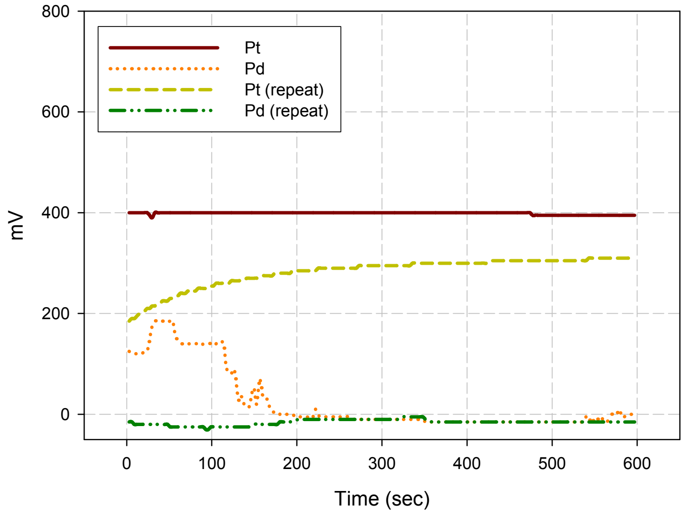


Fig 20 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.5 M SCN$^-$ at pH 2 (not N_2 purged).**

In the absence of O_2, although there are variations between the repeat runs, the trend is again the same with the rest potentials of Pt^0 being greater than that of Pd^0 (figure 21).

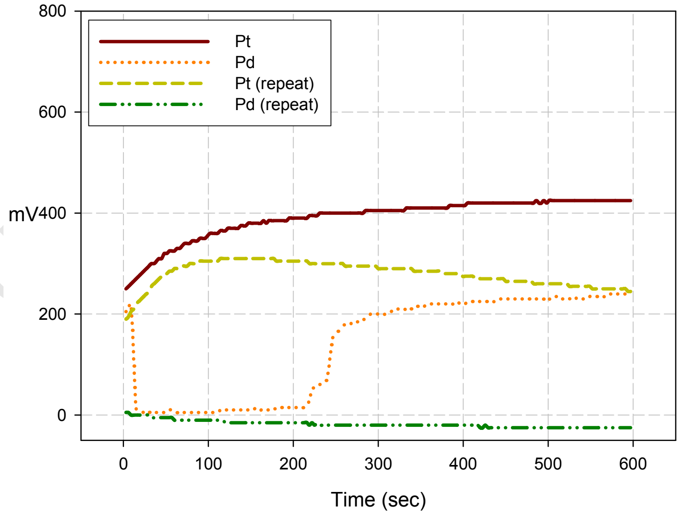


Fig 21 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.5 M SCN$^-$ at pH 2 (N_2 purged).**

The kinetics of dissolution, be it in the presence or absence of O_2 as oxidant (figures 22 and 23), seem to be similar to that at higher pH-values (figure 19). Pd^0, again, shows slightly greater kinetics than Pt^0.

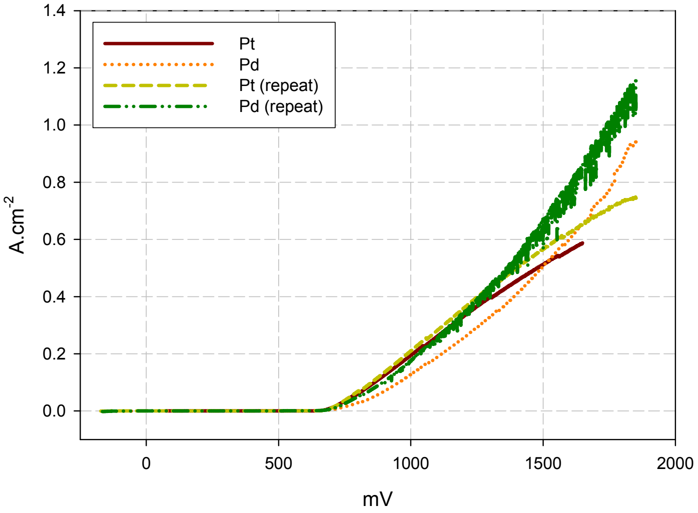


Fig 22 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.5 M SCN$^-$ at pH 2 (not N_2 purged).**

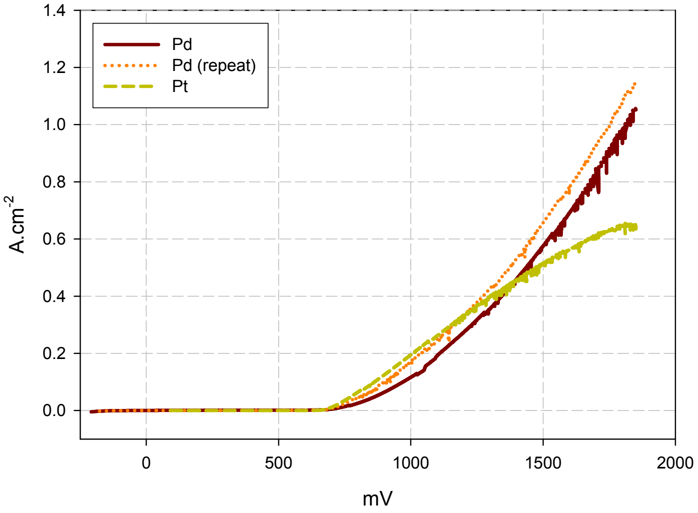


Fig 23 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.5 M SCN$^-$ at pH 2 (N_2 purged).**

4.3.2 Thiosulphate ($S_2O_3^{2-}$) / Oxidant

In the presence of 0.5 M $S_2O_3^{2-}$ and O_2 as oxidant, Pd^0 shows similar rest potential scans at two different electrode rotation speeds, i.e. 200 and 500 rpm (figure 24). This indicates that mass transport control does not come into play. The rest potential for Pt^0 in comparison is lower by approximately 50 mV (figure 25), showing that Pd^0 should be easier to oxidise than Pt^0, which is the direct opposite compared to SCN^-. It is also clear that polishing did not make any difference to the rest potential of Pt^0. In the absence of O_2 the rest potential for Pt^0 remains more or less the same, but that of Pd^0 decreases to below that of Pt^0.

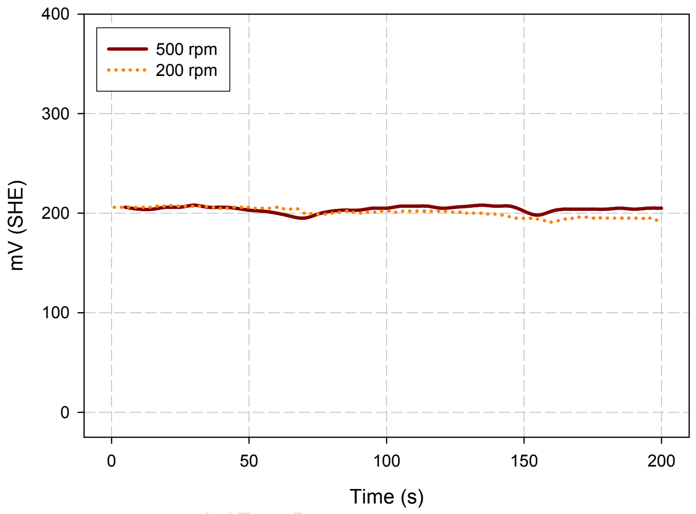


Fig 24 **Rest potential scans for Pd (working electrode) at two rotation speeds in the presence of 0.5 M $S_2O_3^{2-}$ (not N_2 purged).**

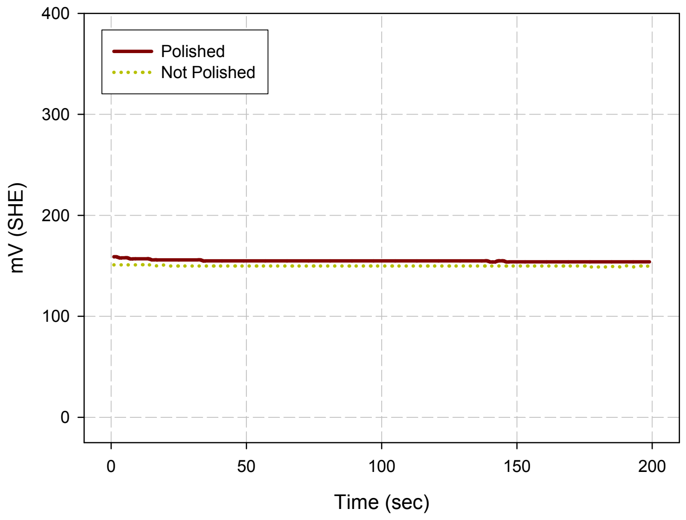


Fig 25 **Rest potential scans for Pt (working electrode) in the presence of 0.5 M $S_2O_3^{2-}$ (not N_2 purged).**

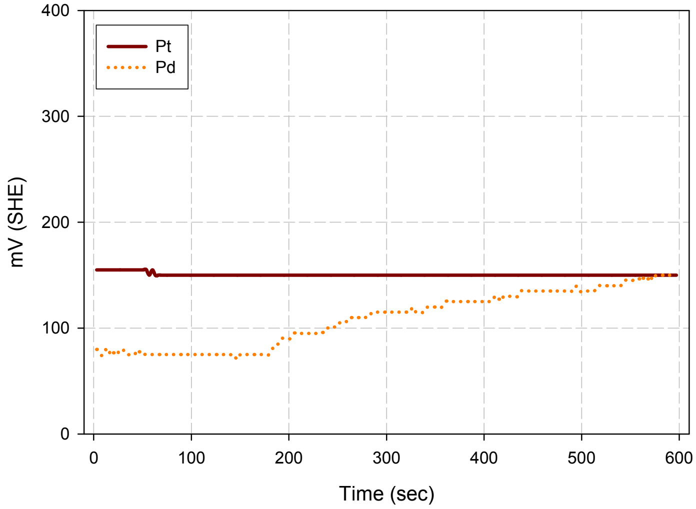


Fig 26 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.5 M $S_2O_3^{2-}$ (N_2 purged).**

The potentiodynamic scans for Pt^0 and Pd^0 show that current is liberated at lower potentials in the case of Pt (figure 27). Pd^0, on the other hand, at 1.2 V, seems to be oxidised at a greater rate compared to Pt^0. Beyond 1.2 V a lot more current is liberated in the case of Pd^0, which could be attributed to the oxidation of H_2O as significant O_2 evolution was observed in the case of Pd^0. No difference is observed in polishing the Pd electrode though.

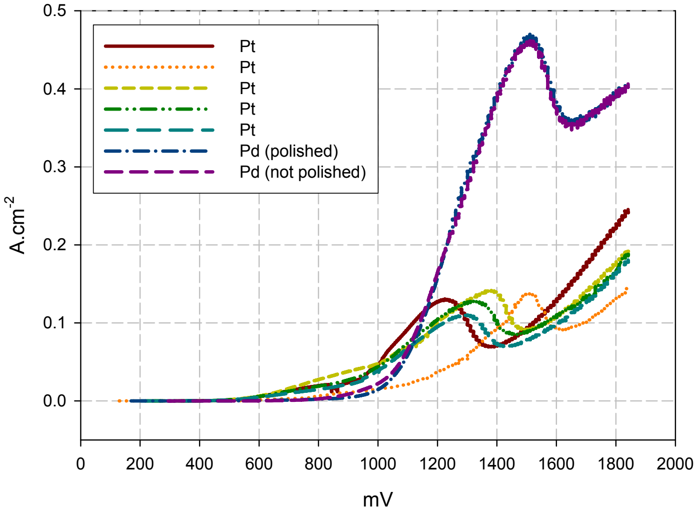


Fig 27 **Potentiodynamic scans for Pt and Pd (working electrode) in the presence of 0.5 M $S_2O_3^{2-}$ (not N_2 purged).**

From figures 28 and 29 it is clear that Pt^0 is oxidised earlier, i.e. at low potential values, compared to Pd^0, but it would seem that the rate of oxidation for Pd^0 picks up at higher potential values.

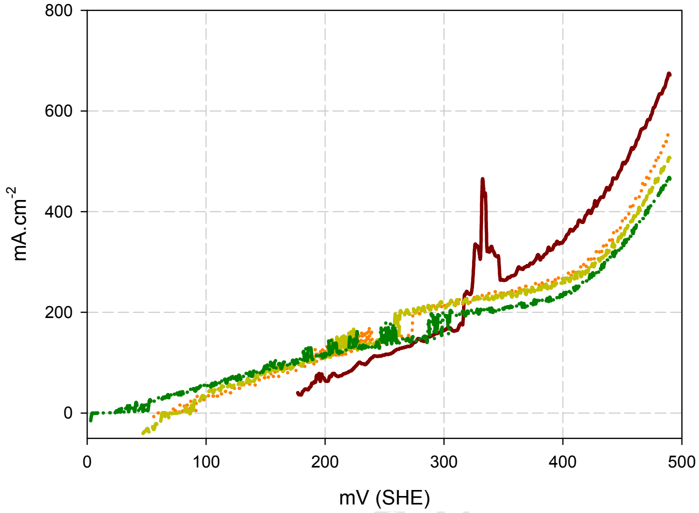


Fig 28 **Potentiodynamic scans for Pt (working electrode) at 1 mV.s^{-1}, with the electrode polished in all instances prior to the scan, in the presence of 0.5 M $S_2O_3^{2-}$ (not N_2 purged).**

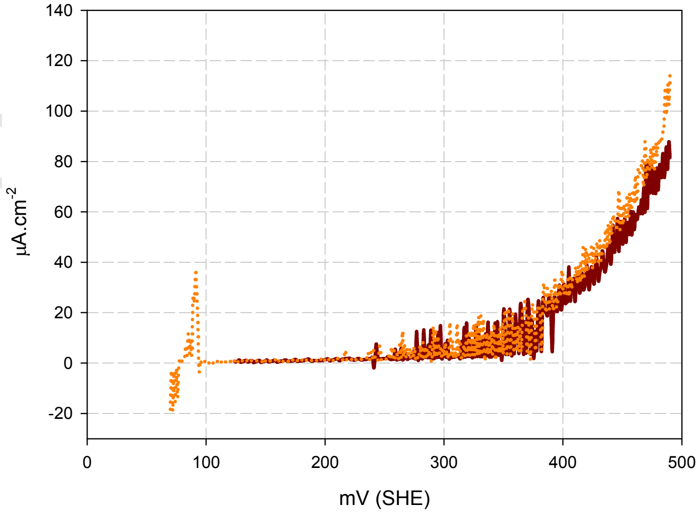


Fig 29 **Potentiodynamic scans for Pd (working electrode) at 1 mV.s^{-1}, with the electrode polished in both instances prior to the scan, in the presence of 0.5 M $S_2O_3^{2-}$ (not N_2 purged).**

In the absence of O_2 (figure 30) the potentiodynamic scans of Pt^0 and Pd^0 show the same trend as in the presence of O_2 (figure 27).

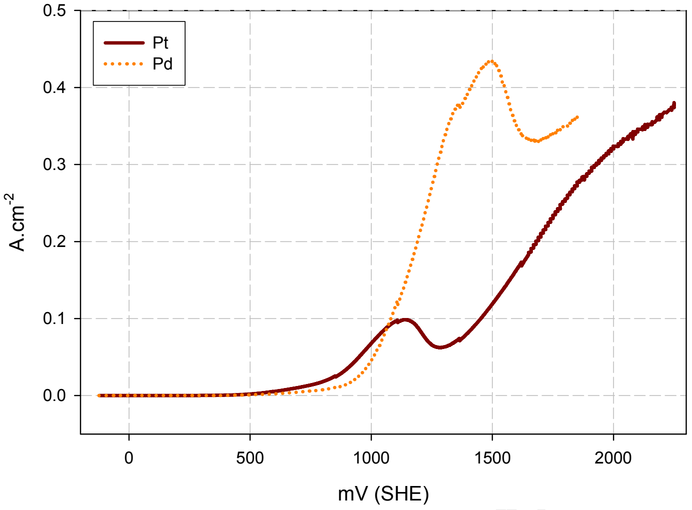


Fig 30 **Potentiodynamic scans for Pt and Pd (working electrodes), at 10 mV.s^{-1}, with the electrode polished in both cases, in the presence of 0.5 M $S_2O_3^{2-}$ (N_2 purged).**

Fixing the pH at 6.27, the rest potentials for Pt^0 and Pd^0 in the absence of any Fe^{3+} (figure 31) and in the presence of Fe^{3+} (figure 32) clearly shows that the rest potential for both metals is increased in the presence of ferric as oxidant.

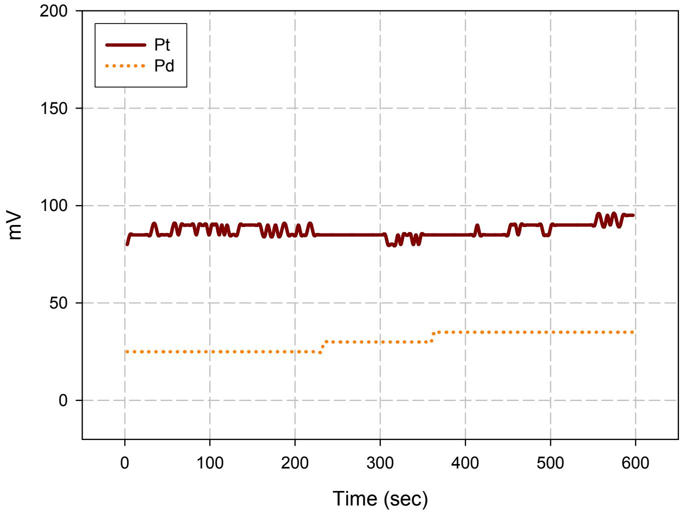


Fig 31 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.5 M $S_2O_3^{2-}$, and no added Fe^{3+}, at pH 6.27 (not N_2**

purged).

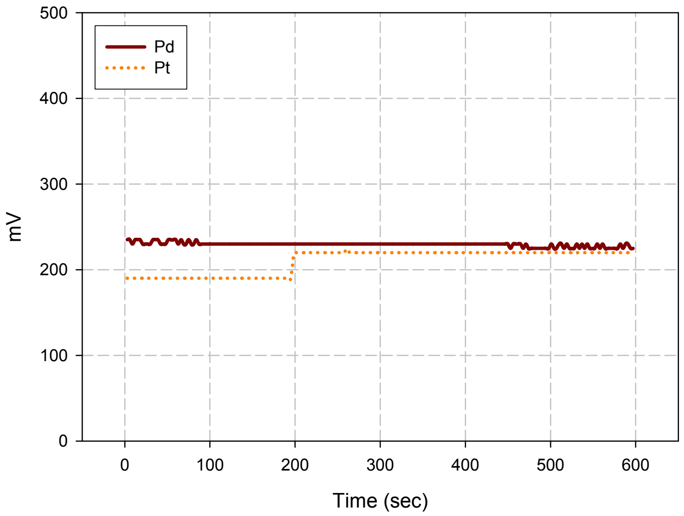


Fig 32 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.5 M $S_2O_3^{2-}$, and added Fe^{3+}, at pH 6.27 (not N_2 purged).**

Although the rest potentials have increased for both metals in the presence of added ferric, the addition of ferric as oxidant did not seem to make any difference to the kinetics of dissolution as the potentiodynamic scans in the absence of ferric (figure 33) and in the presence of ferric (figure 34) are very similar.

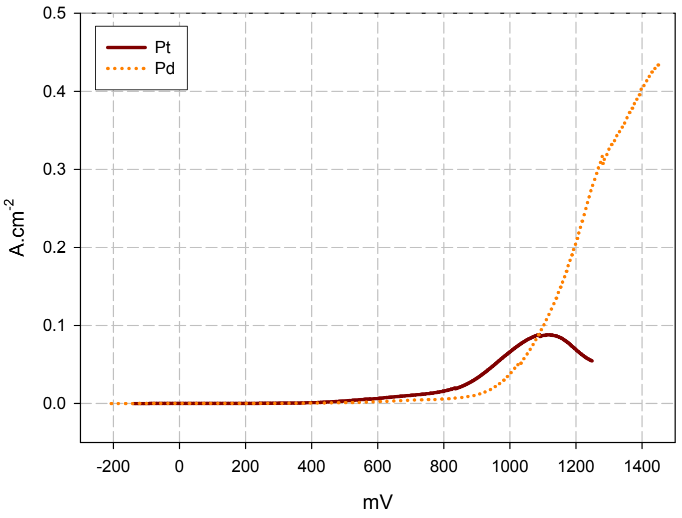


Fig 33 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.5 M $S_2O_3^{2-}$, and no added oxidant, at pH 6.27 (not N_2 purged).**

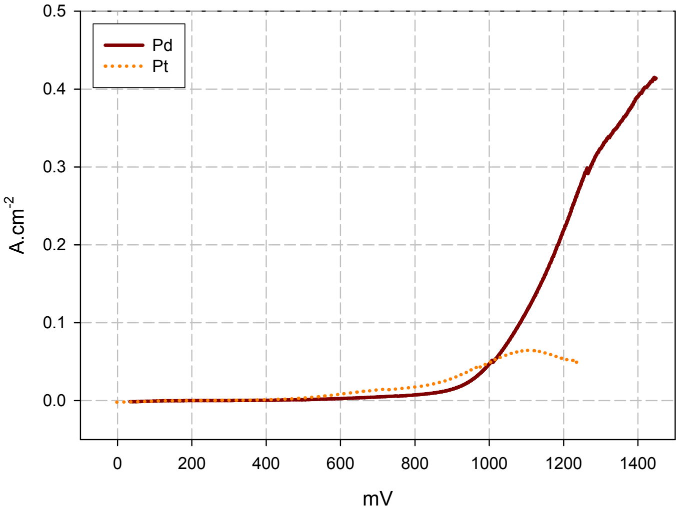


Fig 34 Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.5 M $S_2O_3^{2-}$, and added Fe^{3+}, at pH 6.27 (not N_2 purged).

4.3.3 Thiourea (NH_2CSNH_2) / Oxidant

Similar to thiocyanate, Pt^0 has a greater rest potential than Pd^0 in the presence of 0.5 M thiourea (figure 35). Compared to thiocyanate the rest potential for Pt^0 is more or less the same, whereas that of Pd^0 has decreased.

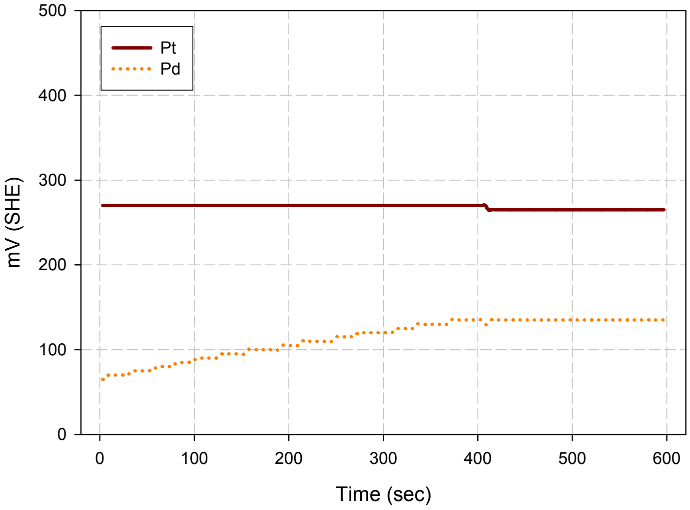


Fig 35 Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.5 M $CS(NH_2)_2$ (N_2 purged).

Lowering the pH to 1.89 sees an increase in the rest potential for Pd^0 to that of Pt^0 in the absence of O_2 (figure 36). In the presence of O_2 though the rest potential decreases with that of Pt^0 to the greatest extent.

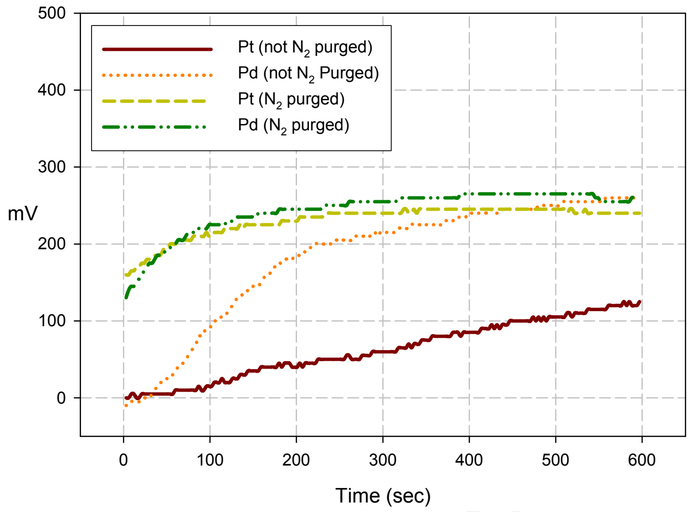


Fig 36 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.5 M $CS(NH_2)_2$ at pH 1.89 (with and without N_2 purging).**

In the absence of any N_2 purging, the presence of ferric as oxidant results in an increase of the rest potential for both metals to greater than 300 mV (figure 37).

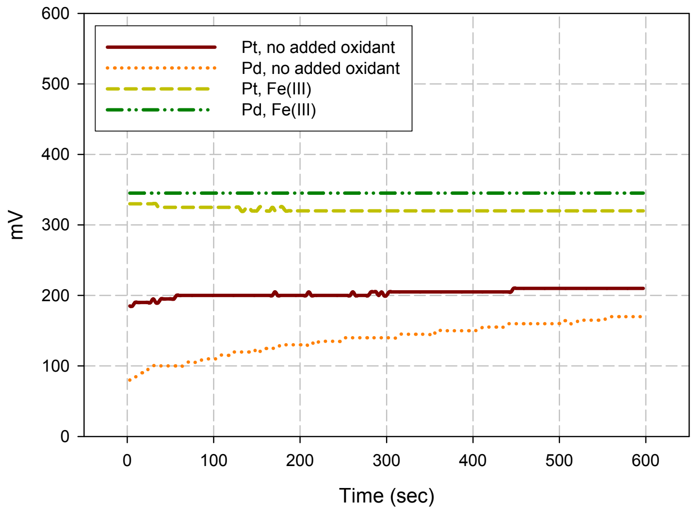


Fig 37 **Rest potential scans for Pt and Pd (working electrodes) in the**

presence of 0.5 M $CS(NH_2)_2$ at pH 1.89 with and without ferric as oxidant (not N_2 purged).

The potentiodynamic scans, however, clearly show that the kinetics of dissolution are extremely slow in the presence of 0.5M thiourea without any O_2 as oxidant as very little current is being liberated (figure 38).

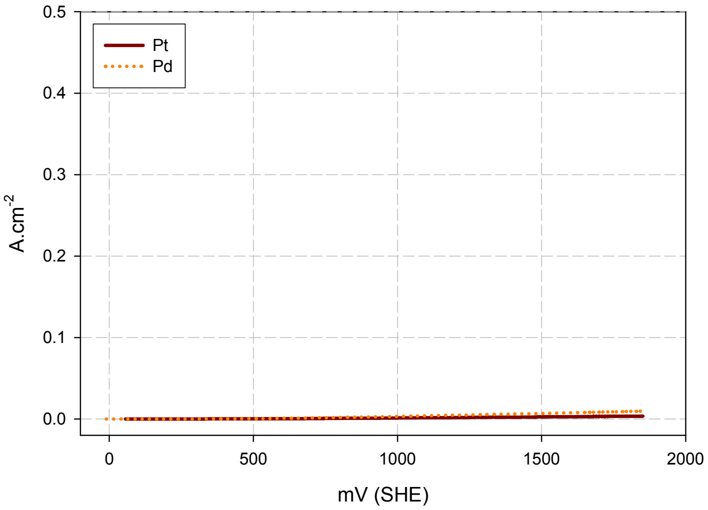


Fig 38 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.5 M $CS(NH_2)_2$ (N_2 purged).**

Lowering the pH to 1.89 has a positive effect on the kinetics of oxidation as the current liberated for both metals are increased (figure 39).

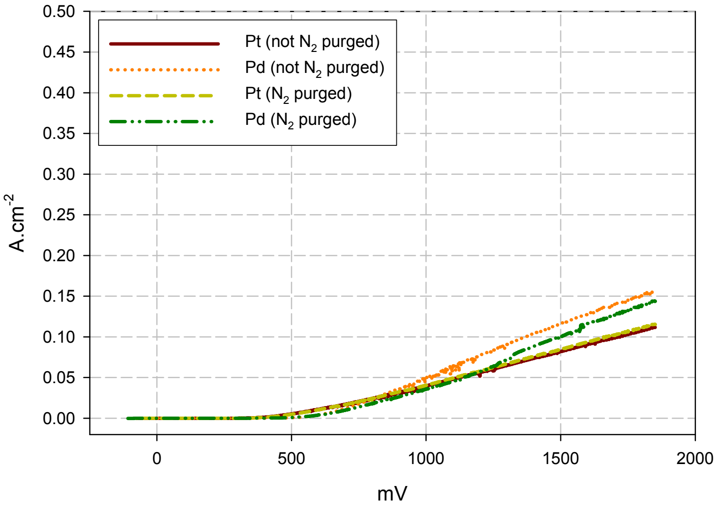


Fig 39 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.5 M $CS(NH_2)_2$ at pH 1.89 (N_2**

purged).

Addition of ferric as oxidant further increases the current (figure 40), but not to the extent of that of thiosulphate (figure 34).

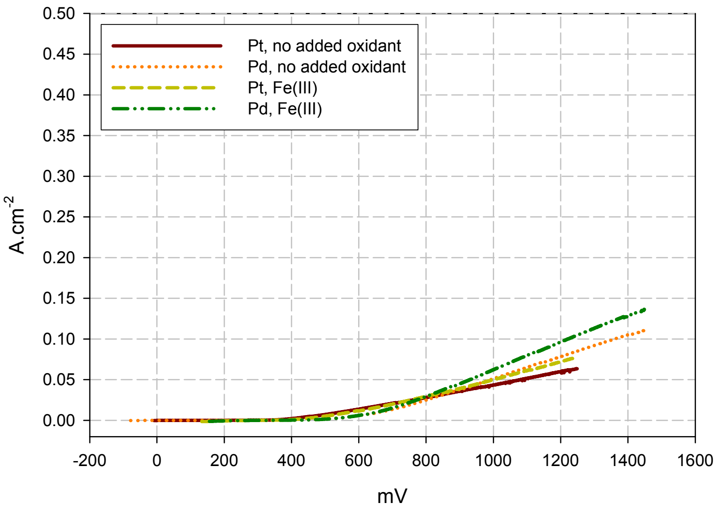


Fig 40 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.5 M $CS(NH_2)_2$, at pH 1.89, with and without ferric as oxidant (not N_2 purged).**

4.3.4 $AlCl_3$ / HCl / Oxidant

With chloride as complexing agent at low pH, i.e. 0.66 M $AlCl_3$ and 10% HCl, the rest potential of platinum is higher than that of palladium, which leads to the expectation that platinum will be easier to oxidise than palladium in a chloride medium (figure 41).

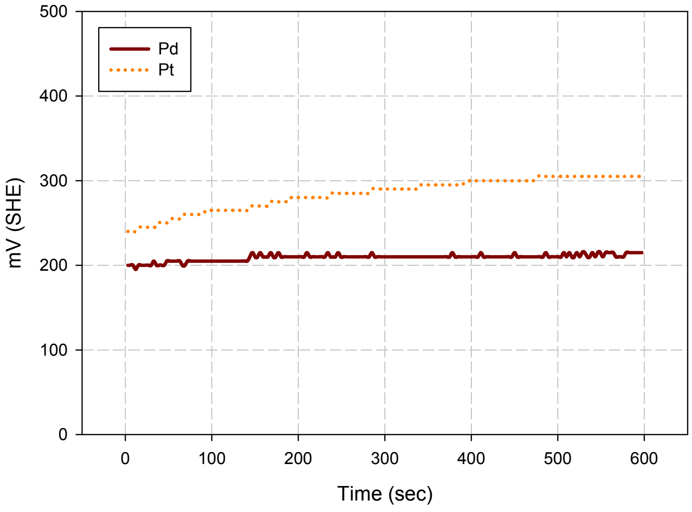


Fig 41 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.66 M $AlCl_3$ / 10% HCl (N_2 purged).**

From figure 42 it is clear that palladium will be oxidised at a higher rate than platinum as current is liberated at a lower potential value for palladium, i.e. approximately 700 mV compared to 1200 mV for platinum.

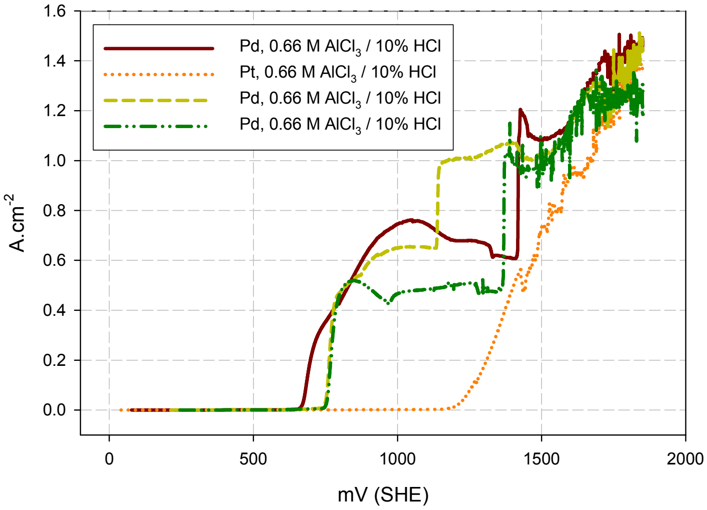


Fig 42 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.66 M AlCl$_3$ / 10% HCl (N_2 purged).**

A stronger electrolytic solution and/or lower pH value results in higher rest potentials for both platinum and palladium, which should result in improved dissolution of both metals (figure 43). Interestingly, however, at 5% HCl palladium now has a higher rest potential.

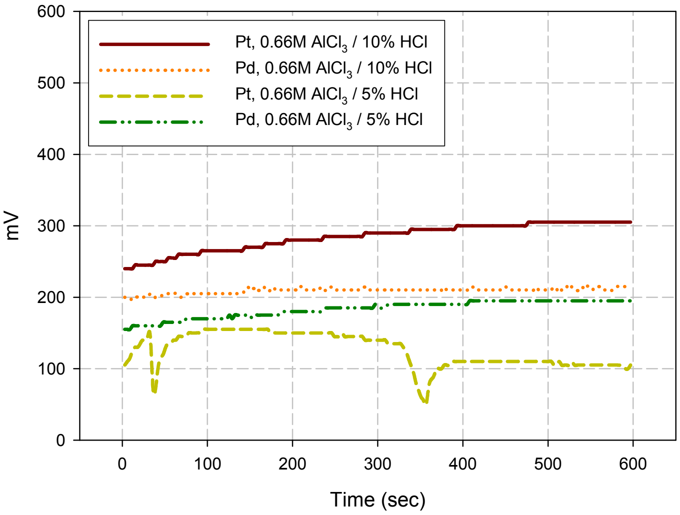


Fig 43 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.66 M AlCl$_3$ / 10% HCl (N_2 purged) and 0.66 M AlCl$_3$ / 5% HCl (N_2 purged).**

The potentiodynamic scans, comparing 5% to 10% HCl, show that palladium dissolves at a higher rate than platinum (figure 44). Furthermore, both palladium and platinum dissolve at lower potential values at higher acid concentrations.

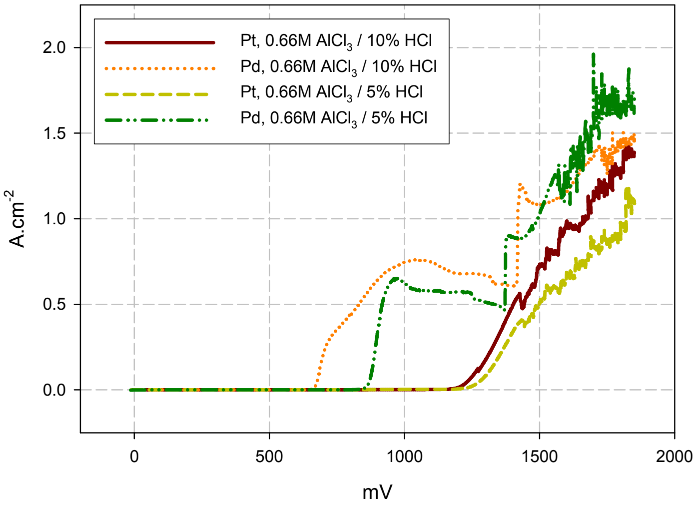


Fig 44 Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.66 M AlCl$_3$ / 10% HCl (N$_2$ purged) and 0.66 M AlCl$_3$ / 5% HCl (N$_2$ purged).

At higher AlCl$_3$-concentrations, 0.66 M vs 0.33 M, palladium seems to be easier to dissolve as the rest potentials are higher for palladium at both concentrations (figure 45). In both instances the higher AlCl$_3$-concentration seems to favour dissolution.

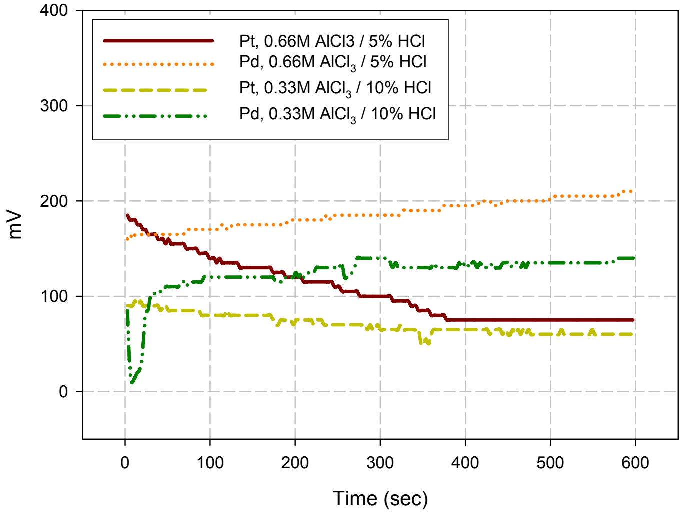


Fig 45 Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.66 M AlCl$_3$ / 5% HCl (not N$_2$ purged) and 0.33 M AlCl$_3$ / 10% HCl (not N$_2$ purged).

At these conditions, in the absence of O_2, the potentiodynamic scans show the same trend with palladium in both instances liberating current at lower potentials with the higher acid concentration liberating current at lower potentials for both palladium and platinum (figure 46).

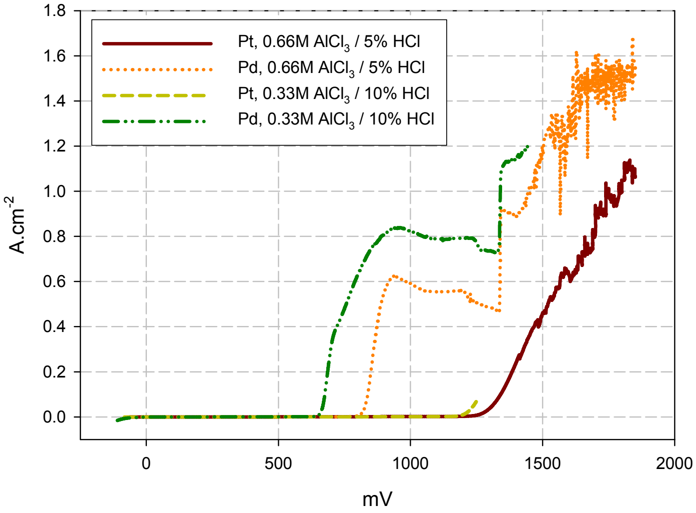


Fig 46 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.66 M $AlCl_3$ / 5% HCl (not N_2 purged) and 0.33 M $AlCl_3$ / 10% HCl (not N_2 purged).**

Addition of an oxidant, in this case sodium hypochlorite, results in the rest potentials for both palladium and platinum to increase drastically with that of platinum being double that of palladium (figure 47). With no oxidant palladium had the higher rest potential though.

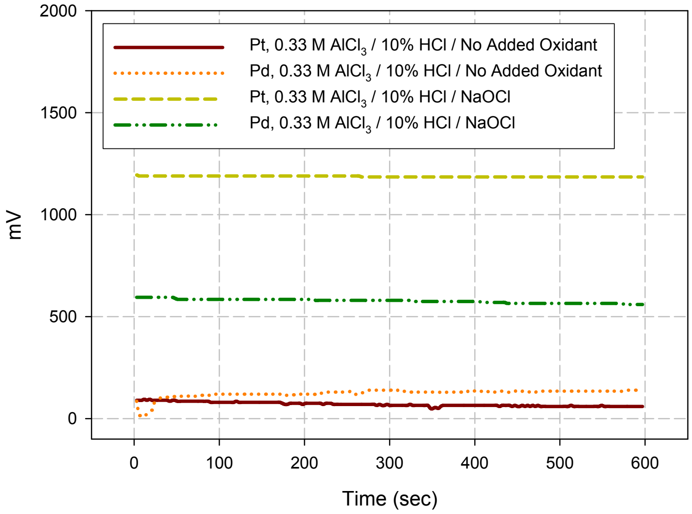


Fig 47 **Rest potential scans for Pt and Pd (working electrodes) in the presence of 0.33 M $AlCl_3$ / 10% HCl / NaOCl (not N_2 purged).**

Although platinum had the highest rest potential in the presence of sodium hypochlorite as oxidant, palladium liberates current at half the potential-value of platinum (figure 48). Even in the absence of an oxidant palladium liberates current at a lower potential than platinum in the presence of an oxidant.

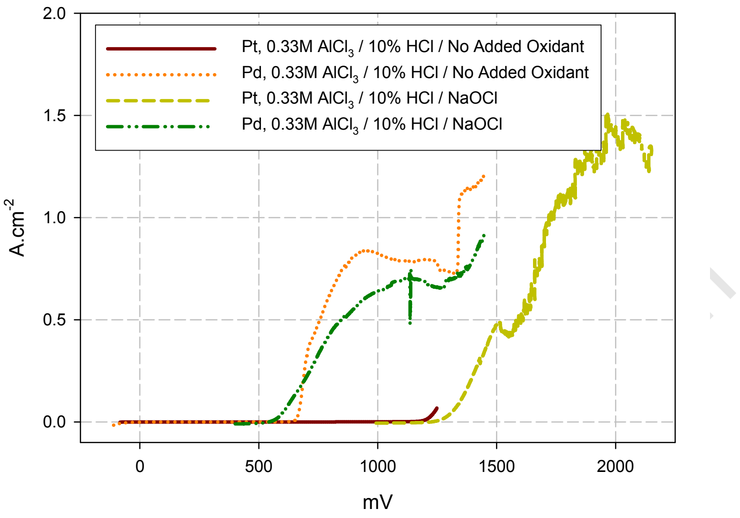


Fig 48 **Potentiodynamic scans for Pt and Pd (working electrodes) at 10 mV.s^{-1} in the presence of 0.33 M AlCl$_3$ / 10% HCl / NaOCl (not N$_2$ purged).**

4.4 Summary

For both platinum and palladium electrochemical data were obtained in the form of rest potential scans (open circuit potential) as well as potentiodynamic scans. These scans were conducted in the absence of oxygen as oxidant (N$_2$ purged), in the presence of oxygen, and in the presence of an additionally added oxidant, i.e. ferric and hypochlorite.

As mentioned previously, the more positive the rest potential for the different oxidizing agents, the better oxidizing agent it would be. From figure 49, for platinum in the absence of any oxidant including oxygen (N$_2$ purged), it is evident that $S_2O_3^{2-}$ and 0.66 M AlCl$_3$ / 10% HCl would be the weakest oxidizing systems, whilst the 0.33 M AlCl$_3$ / 10% HCl system would be the strongest. Both 0.5 M thiocyanate and 0.5 M thiourea seem to be comparable in strength.

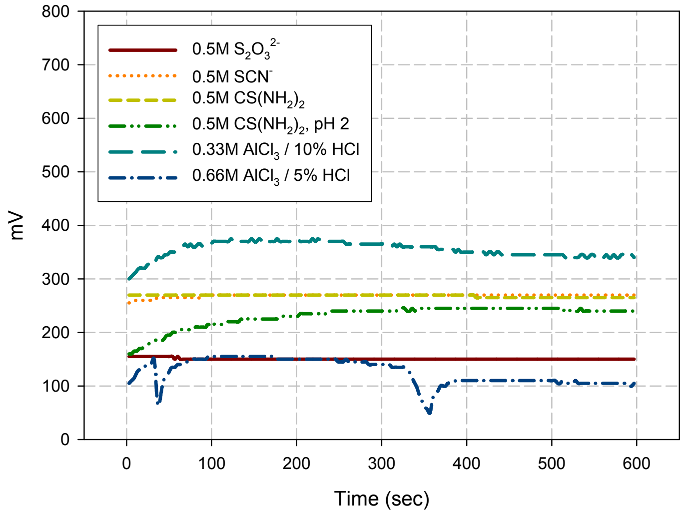


Fig 49 **Rest potential scans for Pt (working electrodes) in the absence of an oxidant (N_2 purged).**

In the presence of oxygen as only oxidant, the 0.5 M SCN^- system had the highest rest potential with the 0.5 M $CS(NH_2)_2$ system at pH 2 the lowest (figure 50). The 0.33 M $AlCl_3$ / 10% HCl system was however not tested under these conditions.

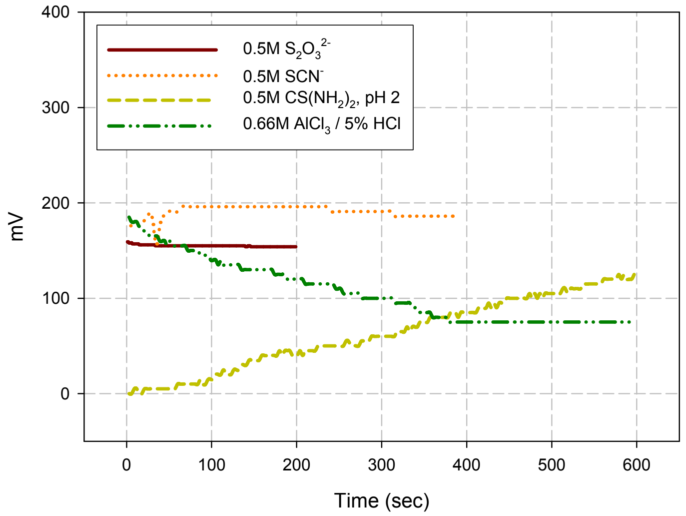


Fig 50 **Rest potential scans for Pt (working electrodes) not N_2 purged. O_2 is therefore the oxidant.**

For palladium (figure 51), in the absence of any oxidant, the 0.5 M $S_2O_3^{2-}$ system still has the lowest rest potential. At time zero the 0.33 M $AlCl_3$ / 5% HCl system has the highest rest potential, but after about 70 seconds the 0.5 M $CS(NH_2)_2$ system at pH 2 overtakes it due to ‘drifting’ of the potential. There is however a clear separation between thiocyanate and thiourea with thiocyanate the stronger. It is furthermore clear that for palladium the rest potentials have shifted to lower values. One however has to take into account the difference between the half-cell reactions for platinum and palladium, before something can be deduced from this shift. In the presence of oxygen (figure 52), 0.5 M $S_2O_3^{2-}$ has the strongest rest potential, which is totally unexpected. The 0.5 M $CS(NH_2)_2$ system at pH 2 again showed extreme drifting.

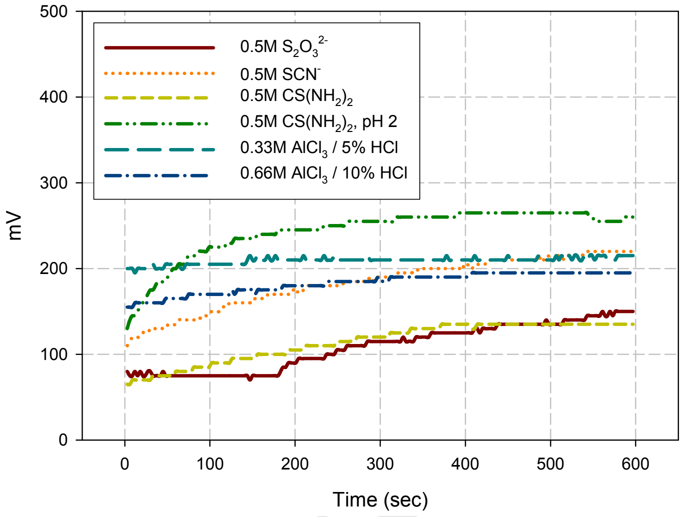


Fig 51 Rest potential scans for Pd (working electrodes) N_2 purged.

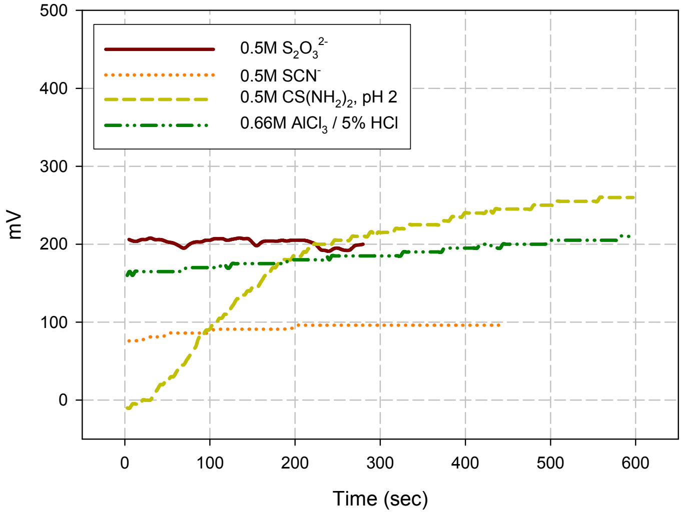


Fig 52 Rest potential scans for Pd (working electrodes) not N_2 purged. O_2 is therefore the oxidant.

In the presence of an added oxidant in the form of ferric ions, the 0.33 M / 10% HCl system at pH 0.31 exhibited the greatest rest potential with regards to platinum (figure 53). It is more than 800 mV greater than the 0.5 M $CS(NH_2)_2$ system at pH 1.89. The $S_2O_3^{2-}$ system at pH 6.27 had the lowest rest potential.

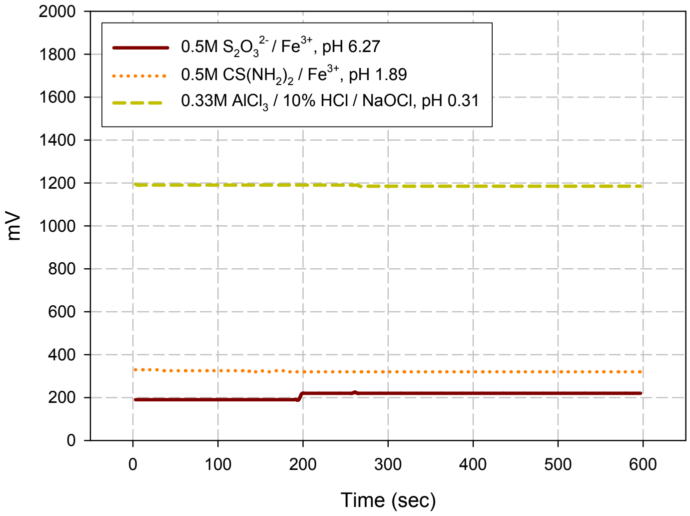


Fig 53 **Rest potential scans for Pt (working electrodes) with added Fe(III). (N_2 purged)**

For palladium the trend is exactly the same as above, but the potential for the 0.33 M / 10% HCl system at pH 0.31 has dropped by half from 1200 mV to 600 mV (figure 54). The thiosulphate system again has the lowest rest potential.

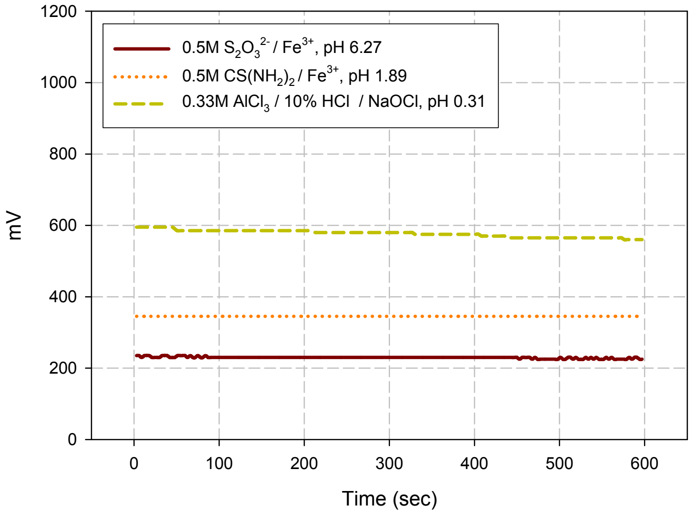


Fig 54 Rest potential scans for Pd (working electrodes) with added Fe(III). (N_2 purged)

Comparing the potentiodynamic scans for each metal, i.e. in the absence and presence of added oxidant, it is very difficult to make any conclusions as the curves are very similar. Furthermore, in many instances the current liberated, at a specific potential in the presence of an oxidant, is even lower than in the absence of this added oxidant (figures 55 – 58).

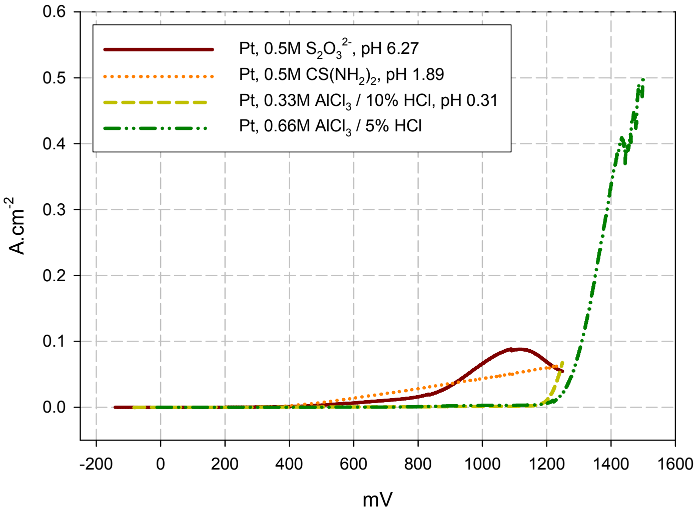


Fig 55 Potentiodynamic scans for Pt (working electrodes) without added oxidant.

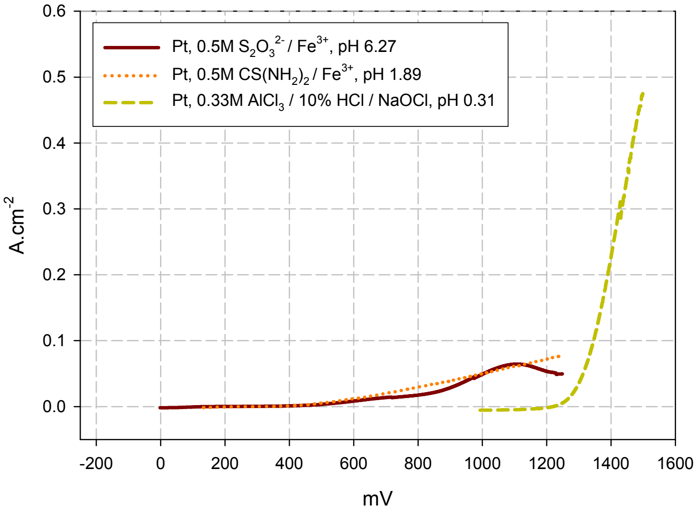


Fig 56 **Potentiodynamic scans for Pt (working electrodes) with added oxidant.**

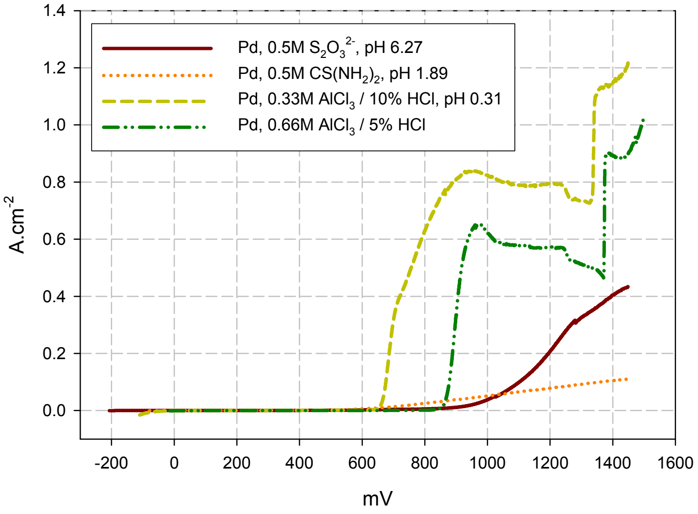


Fig 57 **Potentiodynamic scans for Pd (working electrodes) without added oxidant.**

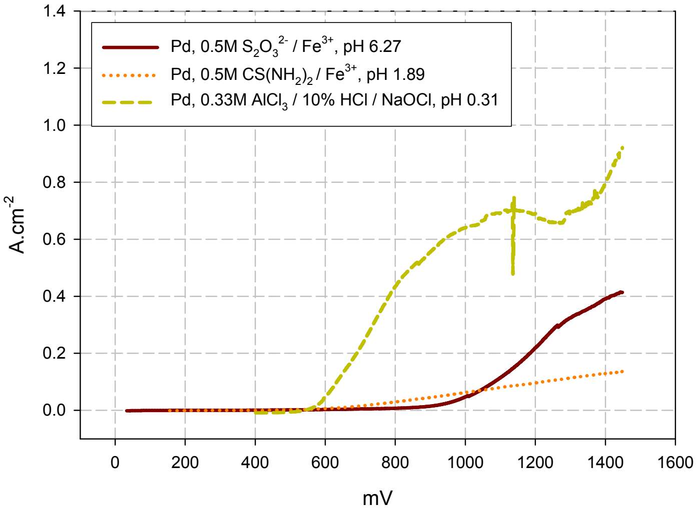


Fig 58 **Potentiodynamic scans for Pd (working electrodes) with added oxidant.**

Based on the insight obtained from the electrochemical investigations, allowing rest potential data to carry a little more weight, one sees that the $S_2O_3^{2-}$ system in many instances has the lowest rest potential. The strongest oxidant system tends to be 0.33 M $AlCl_3$ / 10% HCl / NaOCl. It was therefore decided to subsequently conduct leach runs employing three oxidant systems, i.e. 0.33 M $AlCl_3$ / 10% HCl / NaOCl and 0.5 M SCN^- / Fe^{3+} and 0.5 M $CS(NH_2)_2$ / Fe^{3+}.

Chapter 5

LEACHING

5.1 Introduction

Based on the outcome of the thermodynamic and electrochemical studies it was decided to conduct leach investigations employing the following three lixiviant systems, i.e. $CS(NH_2)_2$ / Fe^{3+}, SCN^- / Fe^{3+}, and $AlCl_3$ / HCl / NaOCl.

The sample material used was virgin catalytic converters supplied by Johnson Matthey's plant in Germiston South Africa. These coated monoliths were crushed and split into three different size fractions, i.e. +2mm, -2+1mm, and -1mm. It was decided to use virgin catalytic converters so as to investigate the leaching of Pt^0, Pd^0 and Rh^0, as spent catalytic converters contain the oxidised form of these metals, e.g. Rh_2O_3, which is more difficult to leach.

5.2 Experimental

All solutions were prepared using deionised water from a Millipore Milli-Q Plus Ultra Pure Water System. Hydrochloric acid (32%, 1L = 1.16kg), sulphuric acid (95%, 1L = 1.84kg), aluminium chloride ($AlCl_3.6H_2O$) and ferric sulphate, $Fe_2(SO_4)_3.xH_2O$ was from Saarchem. Thiourea was from Unilab, and sodium thiocyanate and sodium hypochlorite (11%) from Merck.

The number of moles of water in $Fe_2(SO_4)_3.xH_2O$ was determined spectrophotometrically at 304 nm as the molar extinction coefficient (ε) for ferric is 2197 $M^{-1}cm^{-1}$ at 25°C and does the Lambert-Beer law ($A = \varepsilon.\ell.c$) hold up to 10^{-2}M Fe^{3+} [56]. For an absorbance (A) of 0.65 the required concentration (c) was calculated. A value of x was estimated and the associated mass of salt weighed off and made up to the required volume. The solution was 0.1M with respect to sulphuric acid so as to prevent the hydrolysis of ferric. From the experimental absorbance value the correct concentration value was calculated and the chemical formula calculated as $Fe_2(SO_4)_3.5,863H_2O$.

Sample material of both the -2+1mm and -1mm fractions was sent to Johnson Matthey UK for assay. It was interesting to find that the smaller size fraction, i.e. -1mm, assayed higher for each of the metals. The -2+1mm fraction was however used for all the leach runs. The decision was taken to use the slightly bigger size fraction as earlier investigations have shown that a too small a size fraction (< 500 μm) causes blocking of the packed column. All subsequent results reported are based on the assay conducted by Johnson Matthey UK. Due to a confidentiality agreement signed between Johnson Matthey and the North-West University, the assay results can not be reported and all leach results are therefore reported as percentage recovery.

Lixiviant solutions, $CS(NH_2)_2$ / Fe^{3+} and SCN^- / Fe^{3+}, were prepared and the pH adjusted with sulphuric acid prior to making it up to 500 ml. Subsequent to making the solutions up to 500 ml, the pH was measured with a Thermo Orion 2 Star pH-meter.

Two setups were employed for the leach runs. For both the $CS(NH_2)_2$ / Fe^{3+} and SCN^- / Fe^{3+} systems a batch reactor system was employed as depicted in figure 59. A 700 ml round bottom flask, which fits a 500 ml heating mantle, was used. Its lid allows for an overhead stirrer, a thermometer, and a liebig cooler to curtail excessive evaporation. Once the solution, containing the sample material, reached the required temperature (50°C) it was stirred at ± 300 rpm for 24 hours.

For thiourea two sets of leach runs were conducted, i.e. at 0.3 and 0.6 M thiourea (Tables 5 & 6). For each the ferric-concentration was 0.05, 0.10, and 0.25 M respectively. The sample material was 40g in total, i.e. 15g of the Pt sample and 25g of the Pd & Rh sample.

No	$CS(NH_2)_2$, M	Fe^{3+}, M	Vol., mL	Autocat, g Pt	 Pd & Rh	Time, h	pH	T, °C
S1	0.3	0.05	500	15.0025	25.0017	24	1.78	50
S2	0.3	0.10	500	15.0011	25.0023	24	1.76	50
S3	0.3	0.25	500	15.0010	25.0001	24	1.16	50

Table 5 Conditions for batch leach runs employing 0.3 M $CS(NH_2)_2$.

No	$CS(NH_2)_2$, M	Fe^{3+}, M	Vol., mL	Autocat, g Pt	 Pd & Rh	Time, h	pH	T, °C
S4	0.6	0.05	500	15.0003	25.0003	24	1.12	50
S5	0.6	0.10	500	15.0004	25.0027	24	1.16	50
S6	0.6	0.25	500	15.0008	25.0005	24	1.23	50

Table 6 Conditions for batch leach runs employing 0.6 M $CS(NH_2)_2$.

Fig 59 **Batch leach setup for both the $CS(NH_2)_2/Fe^{3+}$ and SCN^-/Fe^{3+} lixiviant systems.**

For thiocyanate two sets of leach runs were conducted, i.e. at 0.3 and 0.6 M thiocyanate (Tables 7 & 8). For each the ferric-concentration was 0.05, 0.10, and 0.25 M respectively. The sample material was 40g in total, i.e. 15g of the Pt sample and 25g of the Pd & Rh sample.

No	SCN^-, M	Fe^{3+}, M	Vol., mL	Autocat, g		Time, h	pH	T, °C
				Pt	Pd & Rh			
C1	0.3	0.05	500	14.9990	24.9973	24	1.28	50
C2	0.3	0.10	500	15.0036	25.0029	24	1.24	50
C3	0.3	0.25	500	14.9996	25.0037	24	1.24	50

Table 7 **Conditions for batch leach runs employing 0.3 M SCN^-.**

No	SCN$^-$, M	Fe^{3+}, M	Vol., mL	Autocat, g		Time, h	pH	T, °C
				Pt	Pd & Rh			
C4	0.6	0.05	500	14.9966	25.0047	24	1.28	50
C5	0.6	0.10	500	15.0020	25.0023	24	1.21	50
C6	0.6	0.25	500	15.0020	25.0037	24	1.20	50

Table 8 Conditions for batch leach runs employing 0.6 M SCN$^-$.

For the $AlCl_3$ / HCl / NaOCl system a flow through packed column setup was employed as depicted in figure 60. A C23 size liebig cooler was employed as the column. At the bottom the cooler was equipped with a straight port female glass vacuum adapter that was halfway filled with 5-6mm cut glass tubing. On top of the glass tubing pieces 5-6mm glass beads was placed and on top of the glass beads a small piece of glass wool was pushed down the column from the top. The column was then filled with 40g of sample material, i.e. 15g of the Pt sample and 25g of the Pd & Rh sample, that settled on the glass wool. On top of the sample material another piece of glass wool was placed with glass beads on top. A gas-inlet adapter was fitted to the top of the cooler, which allows return of the pumped lixiviant to the reservoir. A thermometer fitting, with thermometer, was fitted to the gas-inlet adapter. All ground glass fittings were joined employing high temperature vacuum grease, which is essential to ensure a tight seal. Teflon coated steel clips were used to keep the fittings in place and keep them from moving away from one another due to the increased pressure as a result of pumping the lixiviant continuously through the cooler. A Lauda waterbath ensured temperature control to both the reservoir and column. The lixiviant, 300 mL of 0.3M $AlCl_3$ and 10% HCl, was allowed to reach temperature in the return-reservoir and then pumped through the column for about 2 minutes before NaOCl was pumped from a non-return reservoir. Two Watson-Marlow peristatic pumps were employed and the pump speed for the return-reservoir was 10Hz whereas the pumpspeed for the non-return reservoir was 7.4Hz. These two solutions met at a t-junction at the bottom of the column where chlorine gas formed, according to equations 31 - 33, and moved up through the column.

$$HCl + NaOCl \rightarrow Cl_2(g) + NaOH \qquad ...31$$

$$HCl + NaOH \rightarrow NaCl + H_2O \qquad ...32$$

$$2HCl + NaOCl \rightarrow Cl_2(g) + NaCl + H_2O \quad \text{(eqn. 31 + eqn. 32)} \qquad ...33$$

Once all of the NaOCl had mixed with the $AlCl_3$ / HCl the solution was circulated through the column for two and a half hours. This solution was then removed and 250 mL of 10% HCl was circulated through the column for 30 minutes to flush the system. This solution was removed and 250 mL of de-ionised water was circulated through the column for 30 minutes and removed. The recovered solution was then made up to 1 L. Three runs were done with 3%, 7%, and 11% NaOCl respectively (Table 9).

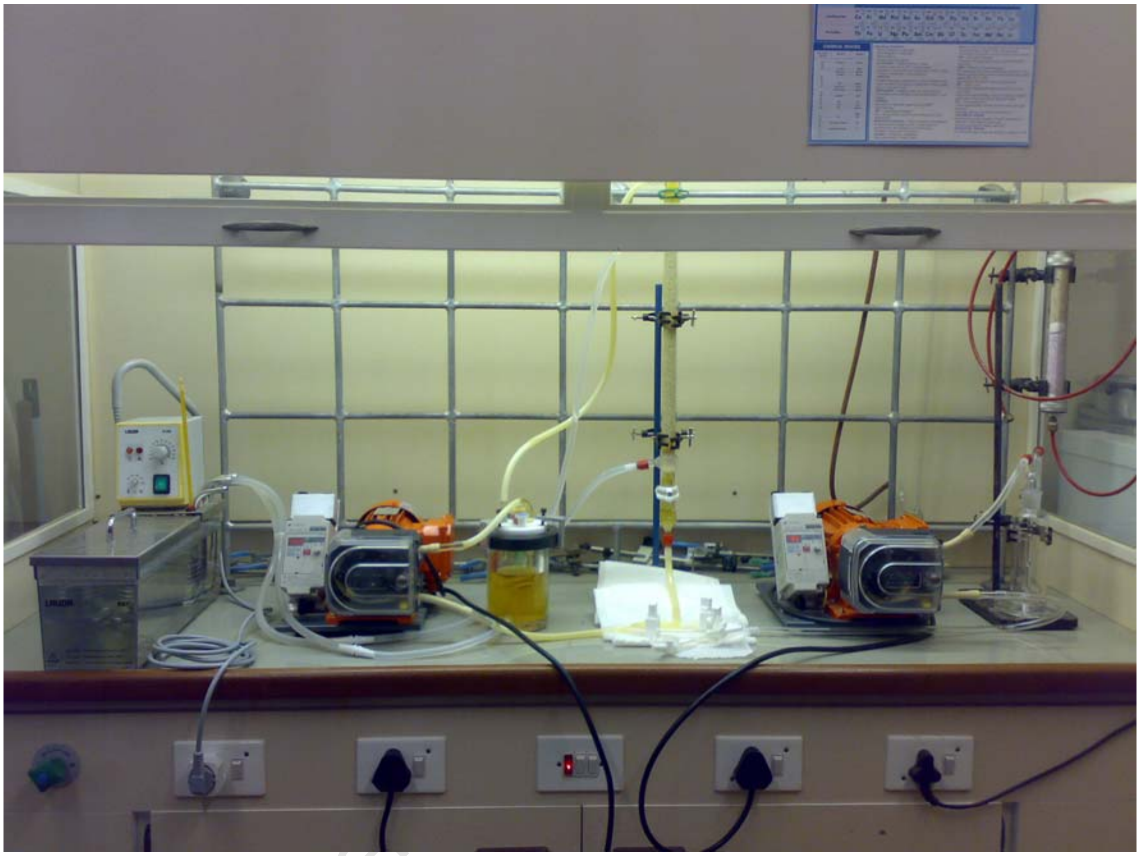


Fig 60 Flow through packed column leach setup for the $AlCl_3$/HCl/NaOCl lixiviant system.

No	$AlCl_3$, M & HCl, %			NaOCl		Autocat, g		Time, h	T, °C
	M	%	mL	%	mL	Pt	Pd & Rh		
A1	0.3	10	300	3	150	25.0038	15.0144	2.5	50
A2	0.3	10	300	7	150	25.0007	15.0033	2.5	50
A3	0.3	10	300	11	150	25.0177	15.0013	2.5	50

Table 9 Conditions for the flow through packed column leach runs.

All solutions, i.e. filtrates, were analysed for PGM content by means of ICP-MS (Inductively Coupled Plasma Mass Spectrometry) employing an Agilent 7500C ICP mass spectrometer.

Solids were not analysed for PGM content subsequent to the leach due to a lack of assaying equipment and are all reported recoveries therefore based on the analysis of solutions by means of ICP-MS with a resolution/precision of parts per billion and less.

5.3 Results & Discussion

5.3.1 SCN^- / Fe^{3+}

For the SCN^- / Fe^{3+} system the results are given in Table 10. For 0.6 M SCN^- and 0.05, 0.10, and 0.25 M Fe^{3+} respectively, the results for the individual metals are fairly close to each other compared to 0.3 M SCN^-. It is however interesting to note that the best result was obtained for 0.3 M SCN^- and 0.25 M Fe^{3+} where, barring experimental errors, 100% of Pd, 92% of Pt, and 32% of Rh was recovered or leached after a 24 hour period. The lowest recovery for Pd was 82% with all the others above 90%. It would therefore seem that Pd forms a fairly stable complex with SCN^-. In the case of Pt the lowest recovery was 56% with all the others in excess of 87% leading one to deduct that Pt also forms a fairly stable complex with SCN^-. For rhodium, however, the recovery varies between 26.9 and 32.6%, which is markedly lower in comparison to both Pd and Pt.

No	% Leached / Recovered		
	Pt	Pd	Rh
C1	56.35	82.54	26.90
C2	87.35	96.95	32.11
C3	92.06	100.10	32.66
C4	89.71	90.72	29.73
C5	91.83	92.51	31.23
C6	90.65	94.98	31.59

Table 10 Results for the batch leach runs employing SCN^- / Fe^{3+}.

From figures 50 and 52 it can be seen that for the SCN^- / O_2 system the open circuit potential for Pt (200 mV) is greater than that for Pd (100 mV), which indicates that SCN^- / O_2 is a stronger oxidant for Pt than for Pd. However, as no run for the open circuit potential of the SCN^- / Fe^{3+} system was conducted no real conclusion can be made. From figure 22 again no formal conclusion can be made as the curves for the potentiodynamic scans of both Pt and Pd are very similar. Current is flowing at 700 mV for both metals.

5.3.2 $CS(NH_2)_2$ / Fe^{3+}

For the $CS(NH_2)_2$ / Fe^{3+} system the results are given in Table 11. For the 0.3 M series and 0.6 M SCN^- series respectively, i.e. for 0.05, 0.10, and 0.25 M Fe^{3+} respectively, the results for the individual metals are not too far off. There does however seem to be a slight improvement for 0.6 M SCN^-. The best result Pd and Rh was obtained for 0.6 M SCN^- and 0.25 M Fe^{3+} where about 18% of Pd and 20% of Rh was recovered or leached after a 24 hour period. For Pt the best result was also obtained at 0.6 M SCN^-, but at a lower ferric concentration of 0.05 M. It is interesting to note, even though recoveries are not that great, that Rh gave the best results in all instances. This is in direct contrast to the SCN^- / Fe^{3+} system where Rh gave the poorest result in all instances.

Having used the same amount of ferric for both the SCN^- / Fe^{3+} and $CS(NH_2)_2$ / Fe^{3+} systems, with the same molar concentrations of SCN^- and $CS(NH_2)_2$, it would therefore be possible to deduce that complex stability as a driving force plays a major contributory role in the leach. However, as the standard reduction potentials for these complexes are not known one is unable to apportion the leaching driving force to the stability of the complexes formed and the 'strength' of the oxidant.

No	**% Leached / Recovered**		
	Pt	**Pd**	**Rh**
S1	1.22	11.96	13.57
S2	1.48	10.51	15.27
S3	1.75	15.41	16.23
S4	2.94	13.26	17.40
S5	2.25	13.99	17.55
S6	2.55	18.15	20.60

Table 11 Results for the batch leach runs employing $CS(NH_2)_2$ / Fe^{3+}.

From figure 37 the open circuit potential (OCP) for the $CS(NH_2)_2$ / Fe^{3+} systems shows that Pd has a OCP at 350 mV compared to that of Pt at 325 mV. However, from the potentiodynamic scan (figure 40) no real conclusion can be made with regard to the kinetics of oxidation as Pt shows more current from 325 – 800 mV with Pd showing more current at potentials higher than 800 mV.

5.3.3 $AlCl_3$ / HCl / NaOCl

For the $AlCl_3$ / HCl / NaOCl system the results are given in Table 12. Leach runs were only conducted for 0.33 M $AlCl_3$, 10% HCl and increasing amounts of NaOCl, i.e. 3, 7 and 11%. It is immediately obvious to note that as the hypochlorite concentration is increased the recovery for each metal decreases. Best recovery is therefore obtained at the lowest hypochlorite concentration used, i.e. 3%. It is furthermore interesting to note that recoveries for both Pd and Rh are very similar, i.e. 60%, with Pt giving the best recovery of 78%. This is in direct contrast to both the previous systems where Pt in every instance gave lower recoveries than Pd. It should be noted that these leach runs were only run for 2.5 hours in comparison to the 24 hours for both the previous systems. As a vertical packed column was employed, with the solution, i.e. lixiviant, pumped from the bottom upwards, the crushed sample material in time settled and compacted to such an extent causing pressure build-up resulting in de-coupling of ground glass joints even with the use of the appropriate size clips to hold the joints in place. It was therefore decided to shorten the leach substantially so as to reduce the risk of possible leakage.

No	**% Leached / Recovered**		
	Pt	**Pd**	**Rh**
A1	78.22	60.10	59.86
A2	69.89	51.18	50.85
A3	62.22	45.27	44.78

Table 12 **Results for the flow through packed column leach runs employing $AlCl_3$ / HCl / NaOCl.**

The open circuit potential (OCP) for the $AlCl_3$ / HCl / NaOCl system (figure 47) indicates an OCP for Pt of 1200 mV compared to 600 mV for Pd. However, from figure 48 it can be seen that for Pd current starts flowing at about 600 mV and for Pt current starts flowing at about 1250 mV. The current flowing for Pt is however not a true reflection of the oxidation of Pt as water is oxidised at 1230 mV and therefore contributes to this current.

The photographs in figure 61 clearly show the extent of leaching with the one on the left taken prior to the leach run and the one on the right taken upon completion of the two and a half hour leach run. Prior to the leach the greyish platinum group metal coating is clearly visible with the majority of it being stripped from the substrate on the right. This stripping, however, could to a large extent be mechanical, i.e. not chemical, as not all of the metal (Pt, Pd and Rh) has been leached. As already mentioned we have not assayed the substrate for PGM content subsequent to the leach as our recovery figures are based on solution analysis and are we interested in the chemical dissolution of the platinum group metal and not the chemical stripping of the platinum group metal from the substrate.

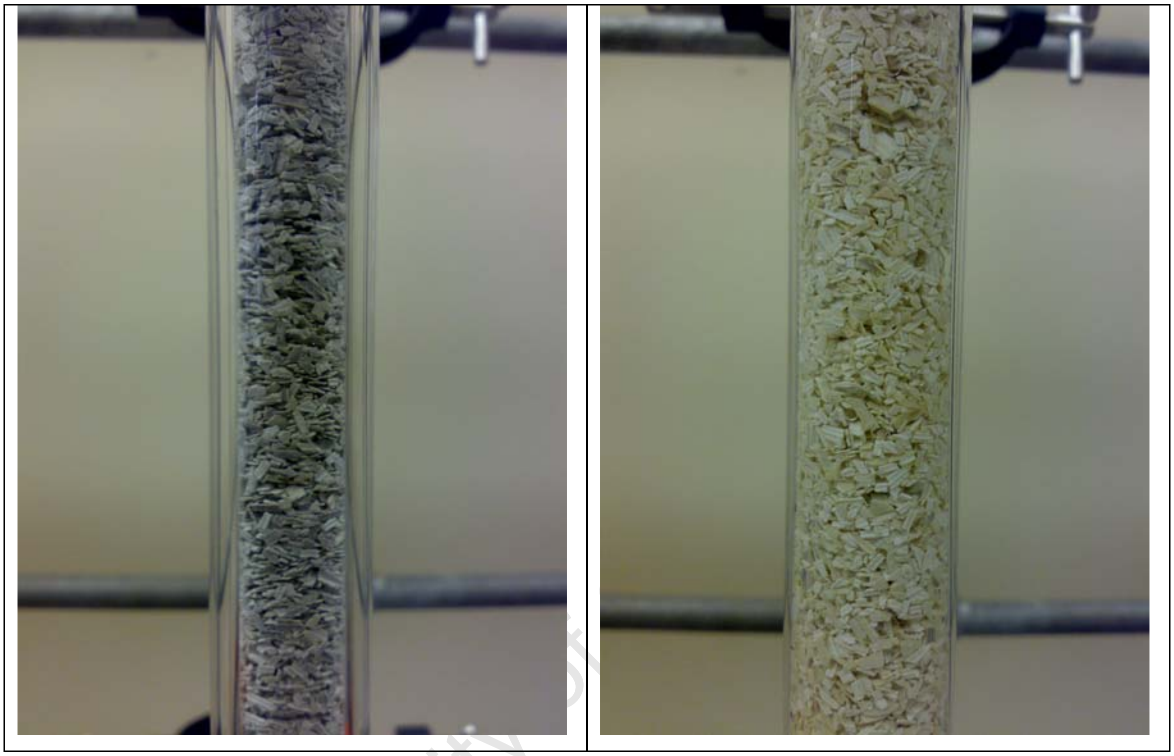


Fig 61 Difference between sample material prior (left) and after (right) a leach run clearly shows the greyish colour of the coated material to the left and the 'stripped' sample to the right.

5.4 Summary

Batch leach runs employing thiourea and ferric, $CS(NH_2)_2$ / Fe^{3+}, did not produce very good recoveries for platinum, palladium and rhodium. What was interesting, however, is that rhodium showed the greatest percentage recovery of the three metals. The batch leach runs employing thiocyanate and ferric, SCN^- / Fe^{3+}, on the other hand produced very good results for both platinum and palladium in the order of 92% and 100% respectively. The packed bed flow-through leach run with aluminium chloride, hydrochloric acid and sodium hypochlorite, $AlCl_3$ / HCl / NaOCl, delivered very promising results for all three metals, i.e. 60% for both palladium and rhodium, and 78% for platinum, given the fact that it was only run for two and a half hours. Indications from literature were such that the $AlCl_3$/HCl/NaOCl system was expected to be a much stronger lixiviant than Fe^{3+}/SCN^- or Fe^{3+}/$CS(NH_2)_2$. It was therefore decided to run the $AlCl_3$/HCl/NaOCl system for a shorter period of time.

Table 13 summarises the order of metal recovery.

Lixiviant System	**Metal Recovery Order**						
SCN^- / Fe^{3+}	Rh	<	Pt	<	Pd		
$CS(NH_2)_2 / Fe^{3+}$			Pt	<	Pd	<	Rh
$AlCl_3$ / HCl / NaOCl	Rh, Pd	<	Pt				

Table 13 Metal recovery order for the three different lixiviant systems.

Only detailed kinetic investigations will shed some light between the correlation of the open circuit potentials and potentiodynamic scans on the one hand and the leach results on the other. Furthermore, solutions should be prepared directly similar to those used for the leach runs and subjected to an electrochemical investigation to be able to draw a direct correlation as the electrochemical investigation conducted as part of this study acted as a scoping or exploratory investigation.

Chapter 6

CONCLUSIONS

Platinum, palladium and rhodium are predominantly being applied as catalysts in catalytic converters of motor vehicles. On average one ton of PGM ore contains roughly about 10 g of total PGM. If we compare this to about 3000 g of PGM per ton of catalytic converter material, it goes without saying that spent catalytic converter material makes for an extremely important secondary source of PGMs. Currently recovery from spent catalytic converters are predominantly being attained by employing pyrometallurgical methods. Two concerns of pyrometallurgy are the high energy costs as well as the associated environmental impacts and concerns. This has resulted in an effort to research possible recovery of PGMs by means of a hydrometallurgical route. However, from the research published it is clear that a lot of time and effort is spent focusing on rather aggressive lixiviant systems, i.e. with regard to the lixiviant used, e.g. aqua regia, as well as the operating conditions, e.g. high pressures and temperatures. Two lixiviants that exhibit good recoveries are aqua regia and cyanide. With aqua regia (HCl/HNO_3) as a lixiviant individual dissolution yields of 98% for Pt and 96% for Pd respectively have been reported, but it suffers from severe loss of oxidising agent (nitric acid) and complexing agent (chlorides) resulting in huge consumption of reagents. Good recoveries have been reported with cyanide (CN^-), e.g. 98% Pt and 99% Pd, but it requires high temperatures and pressures. The problem with aqua regia is being addressed in employing a lixiviant system such as $AlCl_3$ / HCl / HNO_3. This system yields recoveries of 96.6% for Pt and 97.2% for Rh, which is comparable to that of aqua regia, but the great benefit of this system is that it reduces the volume of released gasses by 60%.

As yet no research has been published on employing lixiviants such as thiosulphate ($S_2O_3^{2-}$), thiourea (NH_2CSNH_2), and thiocyanate (SCN^-), which have shown great promise with regard to the dissolution of gold, i.e. 96%, 99% and 95% respectively. These results, and the fact they they are a lot less aggressive, warranted an investigation into the thermodynamics, electrochemistry and leaching of platinum, palladium and rhodium employing these lixiviants.

With regard to the thermodynamic stability of platinum, palladium, and rhodium with these ligands, portrayed in the form of Pourbaix diagrams, it was found that existing data are extremely limited. These diagrams furthermore convey no information regarding the kinetics of oxidation, i.e. conversion from the metallic species to an aqueous species. An in-depth study is required to obtain relevant data on the complexation of Pt, Pd and Rh with $S_2O_3^{2-}$,

NH_2CSNH_2, and SCN^-, in order to portray a more realistic or true picture of the different stability regions.

Based on the insight obtained from the electrochemical investigations, allowing rest potential data to carry a little more weight, one sees that the $S_2O_3^{2-}$ system in many instances has the lowest rest potential. The strongest oxidant system tends to be 0.33 M $AlCl_3$ / 10% HCl / NaOCl. It was therefore decided to subsequently conduct leach runs employing three oxidant systems, i.e. 0.33 M $AlCl_3$ / 10% HCl / NaOCl and 0.5 M SCN^- / Fe^{3+} and 0.5 M $CS(NH_2)_2$ / Fe^{3+}.

It was interesting to observe that, although thiourea and ferric, $CS(NH_2)_2$ / Fe^{3+}, does not seem to be an effective lixiviant for PGM leaching, it leached rhodium to a greater extent compared to platinum and palladium. Thiocyanate and ferric, SCN^- / Fe^{3+}, would seem to be a good lixiviant delivering good results for both platinum (92 % recovery) and palladium (100 % recovery) and would certainly warrant further investigation. Aluminium chloride, hydrochloric acid and sodium hypochlorite, $AlCl_3$ / HCl / NaOCl, produced promising results for all three metals, i.e. 60% for both palladium and rhodium, and 78% for platinum. It also warrants further detailed investigation as it was only run for two and a half hours, compared to the twenty-four hour runs for $CS(NH_2)_2$ / Fe^{3+} and SCN^- / Fe^{3+}.

Detailed kinetic investigations should be conducted to correlate the open circuit potentials and potentiodynamic scans on the one hand and the leach results on the other. This will also aid the development of an optimised hydrometallurgical recovery process.

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