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# AMMONIUM HEXACHLORORUTHENATE PRECIPITATION

**MSc Thesis – Hydrometallurgy**

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**University of Cape Town**

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**AMMONIUM HEXACHLORORUTHENATE PRECIPITATION**

**MSc Thesis – Hydrometallurgy**

**59 pages, 1 Appendices**

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**ABSTRACT**

Ammonium hexachlororuthenate (ACR) is a salt precipitated during a substitution reaction between ammonium and ruthenate dissolved in a strong hydrochloric acid medium. This precipitation reaction is used within the platinum industry as a means of recovering and purifying ruthenium. Application of this process at the Precious Metals Refinery of Anglo Platinum has brought to light certain inefficiencies. In recent years, volatility in the Ru market price occurred, indicating a potential to benefit financially from an improved Ru recovery. Consequently, this study was conducted to understand the effect of certain parameters on the process of precipitating ammonium hexachlororuthenate.

The objective of this study was to improve the yield of the process and also to gain a better understanding of the chemistry and mechanisms involved in this precipitation process.

Experimental work on a scale of 1 litre was conducted in a laboratory. Precipitation experiments were conducted in which the following different parameters were varied independently from one another:

- Longer time feed liquor spent at boiling temperatures;
- Increasing the stoichiometric excess of  $\text{NH}_4\text{Cl}$ ;

- Increasing the operating temperature and reaction time;
- Higher Ru feed concentration;
- Addition of H<sub>2</sub>O<sub>2</sub> as an oxidant.

Each experimental variation was run in four replicate experiments. These results were compared against a base case. Additional analysis was done to determine the species present. The solubility of ACR was also experimentally determined at various HCl and NH<sub>4</sub>Cl concentrations.

The main findings were as follows:

- The most dominant specie present in the effluent is the dimer. No Ru(III) species were detectable in the speciation profiles.
- The dimer has a higher solubility than that of the monomer and limits the extent of precipitating ACR.
- A decrease in yield of 0.45 % is significantly noticeable when the liquor is evaporated for 6 hrs compared to 1.5 hours in the base case. Extensive reaction time at high temperatures promotes the formation of the dimer specie and subsequently decreases the yield.
- All other interventions as listed above did not result in significant changes of the ruthenium yield within the range of each of the specific parameters that were varied.
- Faster addition of NH<sub>4</sub>Cl and precipitating at a higher temperature promotes formation of smaller particles.
- ACR is soluble in water but its solubility decreases as the acid concentration increases. The ACR solubility decreases even further in the presence of NH<sub>4</sub>Cl.

Further test work is recommended to understand and control the equilibrium of the monomer to dimer reaction. Work should also be conducted testing the hypothesis that ACR re-dissolves after precipitation.

**Keywords:** Ruthenium, speciation, [Ru<sub>2</sub>OCl<sub>10</sub>]<sup>4-</sup>, [Ru(H<sub>2</sub>O)Cl<sub>5</sub>]<sup>2-</sup>, [RuCl<sub>6</sub>]<sup>2-</sup>, ammonium hexachlororuthenate, precipitation, supersaturation

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## Abbreviations

Symbol	Description
ACR	Ammonium hexachlororuthenate
AES	Atomic emission spectrometry
FICO	Final concentrate
HCl	Hydrochloric acid
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
NH <sub>4</sub> Cl	Ammonium chloride
NHE	Normal hydrogen electrode
(NH <sub>4</sub> ) <sub>2</sub> RuCl <sub>6</sub>	Ammonium hexachlororuthenate
PGM	Platinum Group Metal
PMR	Platinum Metals Refineries
PSD	Particle size distribution
Ru	Ruthenium
[RuCl <sub>6</sub> ] <sup>2-</sup>	Hexachlororuthenate
[Ru <sub>2</sub> OCl <sub>5</sub> ] <sup>4-</sup>	Dimer-hexachlororuthenate
[RuCl <sub>5</sub> (H <sub>2</sub> O)] <sup>2-</sup>	Pentachlororuthenate
RuO <sub>4</sub>	Ruthenium tetroxide
RuO <sub>2</sub>	Ruthenium dioxide
RuO <sub>4</sub>	Ruthenium tetroxide

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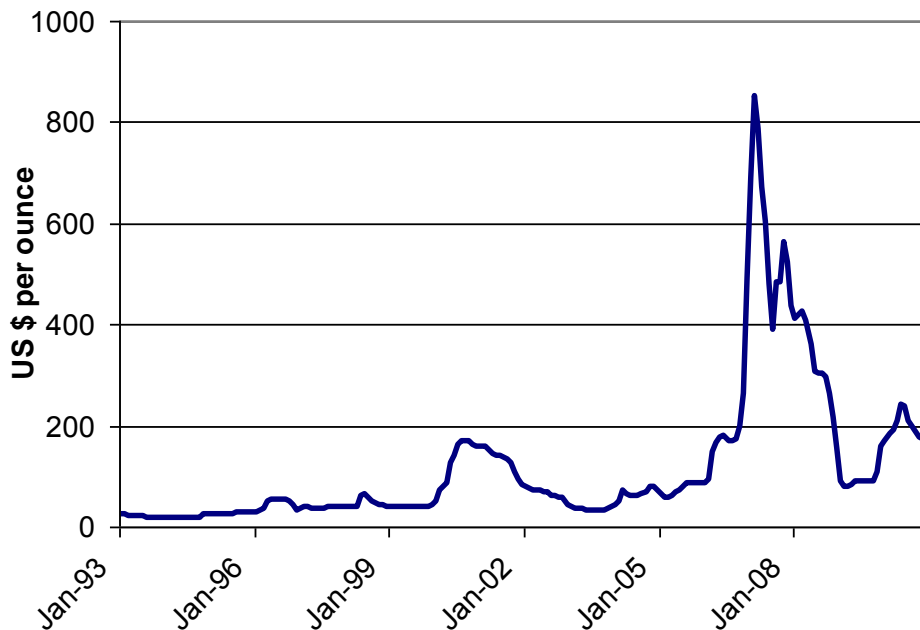
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# 1 INTRODUCTION

Ruthenium is one of the platinum group metals (PGMs) that has shown considerable potential in recent years to be as profitable as the other precious metals. The current average ruthenium price (December 2010) is just over \$ 170 per troy oz but in 2006 it tripled within 4 months (see Figure 1). The main reason for the sudden increase in 2006 was the potential use of this metal in electronic hard disk storage applications (Anglo Platinum annual report, 2006). The subsequent drop in price can be attributed to volatility in the market and the development of competing technologies not reliant on ruthenium. The current price, although lower than in 2006 is still reasonably high. In light of the current state of the ruthenium market it is worthwhile to investigate and eliminate any possible areas where ruthenium losses can occur. These processes should be optimised in order to achieve maximum profit/revenue.



**Figure 1: Average ruthenium prices from 2003 to 2010 ([www.platinum.matthey.com](http://www.platinum.matthey.com))**

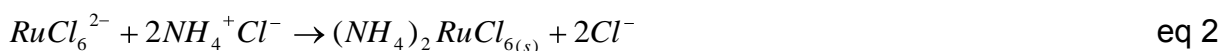
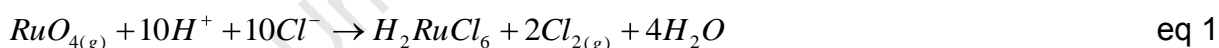
Ruthenium (Ru) is used in various applications including electrical contacts, auto-catalysts, jewellery and in the medical industry. Ruthenium is one of the metals produced by the Precious Metals Refinery (PMR) of Anglo Platinum. The Ru produced at the PMR is in the form of metal and is a favourite in the global ruthenium market due to the crystal size and morphology of the sponge (Hagemann, 2008). The PMR is situated in Rustenburg, South Africa. It is the last processing step in the PGM mine-to-metals beneficiation chain where

PGMs are refined from a mixed metal concentrate to high purity metal products. Ruthenium is one of these products and is produced at purities greater than 99.97 %.

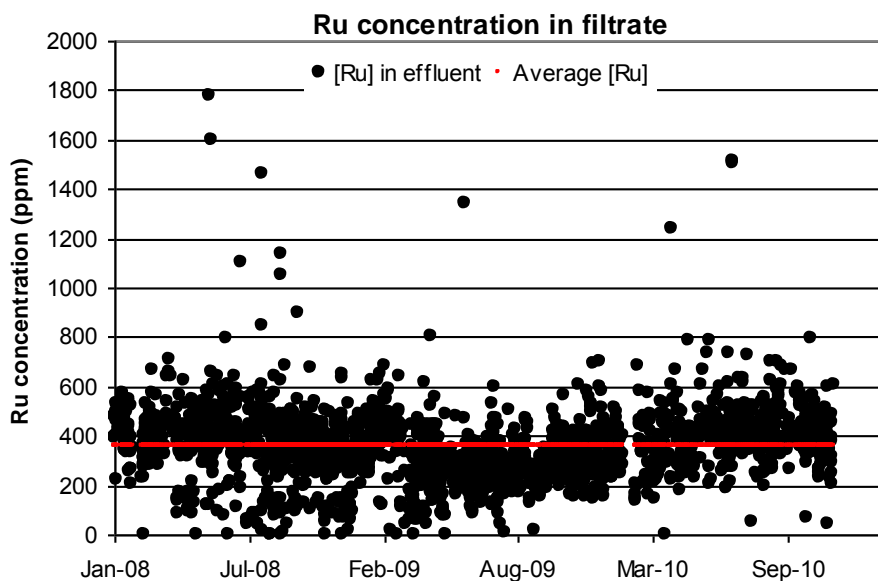
To achieve such purity at the PMR, the metal has to be separated from the other PGMs in the initial leach liquor in which the concentrate is dissolved and subsequently purified in the ruthenium side stream process before final reduction.

The industrial operation at the PMR selectively uses the (VIII) and (IV) oxidation states of ruthenium in the separation and purification stages. Ruthenium is separated from the remaining PGMs in the core leach liquor by volatilising it as ruthenium tetroxide gas ( $Ru(VIII)O_{4(g)}$ ).  $RuO_{4(g)}$  is adsorbed in 6 M HCl through a scrubbing process (equation 1). The scrub acid is at a fixed volume (~ 800 lts) and as soon as it is depleted (HCl molarity less than 3.5 M) the Ru rich liquor is transferred as a batch to the side stream process for purification.

The Ru concentration of this liquor is approximately 25 g/l (i.e. 20 kg per batch). The Ru concentration is increased to  $\pm 45$  g/l by boiling for approximately four hours. The molarity of HCl is increased through boiling the liquor to the azeotropic point at 5.8 M (~ 6 M) HCl at standard pressure. The liquor is cooled to 85 °C and a saturated ammonium chloride solution (250 g/l) is added at an addition rate of 400 litres per hour. An excess amount of 1.5 times that of the stoichiometric requirement is added (i.e  $\pm 220$  litres  $NH_4Cl$  solution). Ammonium hexachlororuthenate (ACR),  $(NH_4)_2RuCl_6$ , is precipitated (shown by equation 2) and filtered, before it is transferred to the downstream process for calcination and final reduction.



Historic operational data for the period January 2008 to November 2010 shows that the average yield of this process is 98.2 % (Figure 2). This yield corresponds to a residual Ru concentration in the filtrate of 354 ppm, with a standard deviation of  $\pm 150$  ppm. The annual loss of Ru to the effluent treatment plant as a result of this process inefficiency is 175 kg Ru.



**Figure 2: Plant data showing Ru concentration in the effluent after the ACR precipitation process**

Further processing of the Ru effluent does recover most of this loss, but there is an extended pipeline and revenue loss associated with the effluent recovery of Ru and hence not desirable. Improvement of the precipitation yield is difficult but possible and the financial implication of an improvement of even just 0.5 % points could be substantial especially at an increased Ru market price. A better understanding of the fundamental chemistry and speciation around this processing step would therefore aid in the development of more efficient processes in the future refining of Ru.

The objective of this study is to improve the precipitation yield by attempting to understand and manipulate some of the parameters that potentially limit the reaction. A number of hypotheses was investigated in this study, as follows:

- The yield of precipitation will decrease if the feed liquor is kept at boiling temperatures for longer periods. The liquor is boiled prior to the precipitation to increase the Ru concentration to ~ 45 g/l. If the liquor is kept longer at boiling temperatures to achieve this concentration, the yield will decrease. It is hypothesized that this occurs because different Ru species form when the liquor is exposed to high temperatures and these species do not precipitate with  $\text{NH}_4\text{Cl}$ , or because the ammonium-ruthenium species that form have a higher solubility than that of ACR.

- Higher operating temperatures during  $\text{NH}_4\text{Cl}$  addition and subsequent ACR precipitation will increase the yield of ACR. It is hypothesized that the reaction is kinetically controlled and that higher temperatures will increase the kinetics of the reaction and therefore the conversion to ACR.
- The yield is governed by supersaturation, Hence, increasing the starting concentration prior to precipitation will improve the yield. The hypothesis is that if the ruthenate reagent is at a higher concentration, the degree of supersaturation is higher and more Ru will precipitate.
- Increasing the amount of reagent added will increase the yield due to not enough reagent being present for the reaction to complete under present conditions.
- Addition of hydrogen peroxide as an oxidant prior to precipitation will ensure that the only species present are the Ru(IV) species. Therefore, other species (especially Ru(III)) that potentially do not precipitate with  $\text{NH}_4\text{Cl}$ , or have higher solubilities, will not be present and this will subsequently improve the yield.

A critical constraint when changing any parameters is the size of the final ruthenium sponge crystal. Any changes recommended in this work should not change the crystal size significantly. A decrease in particle size is undesired due to a market demand for a specific Ru sponge structure. Another reason is that fine particles potentially result in downstream capacity constraints through long filtration times. This study only takes into account Ru species in a chloride medium and the precipitation of ACR with ammonium chloride. It is also limited to varying parameters within ranges that are practically possible at the PMR.

## 2 LITERATURE REVIEW

### 2.1 Ruthenium in general

Ruthenium's history dates back from as early as 1804 when a blue solution was formed as platinum metals reacted with zinc. However, at the time it was attributed to the element iridium (Ir). In 1827 Osann claimed the discovery of Ruthen but later withdrew the claim as the same results could not be reproduced. It was officially discovered by Russian scientist Karl Karlovich Klaus in 1844. Klaus named the substance ruthenium out of respect for Osann's pioneering work. The name is also related to his country, Russia, of which the medieval name was Ruthenia (Seddon & Seddon, 1984).

Ruthenium, osmium, rhodium and iridium are also known as the insoluble PGMs, as these dissolve much more slowly than palladium and platinum and only in the presence of stronger oxidising agents. PGMs form complexes with many different elements in aqueous solution, but the chloro complexes are most studied, as solution in chloride is the only cost effective way for purifying these metals (Bernardis, Grant & Sherrington, 2005).

Ruthenium metal is hard and brittle and therefore barely workable. Ru is very valuable as part of alloys and also as part of catalysts. 50 % of the world demand comes from the electrical industry where ruthenium is added to Pt and Pd for the use of electrical contacts. 40 % is used in the catalyst industry. There are two properties that make Ru useful in alloys. The first is the tendency to harden the alloy and the second is that it makes the alloy resistant to chemical attack. Only 0.1 % Ru in titanium alloy makes it 100 times more corrosion resistant (<http://platinum.preciousmetalinvestment.com>)

Ru is also used in the medical industry as part of anti-malarial, antibiotic and immunosuppressive drugs and has recently appeared also in cancer preventative drugs. The main properties that make Ru unique and well suited for medical drug applications are: (Allardyce & Dyson, 2001)

- Rate of ligand change
- Range of accessible oxidation states
- Ru can mimic iron on how it binds to various biological molecules

Other uses include jewellery, pen tips, fuel cells and hard disk magnetic storage.

## 2.2 Typical PGM refining

PGMs are a scarce resource and the mining of the PGMs are complex as the relevant ore seams sit far below surface and are less than 1 m thick. Therefore the mining cost surrounding PGM production is significant. The main known deposits of PGMs are in South Africa, Russia and Zimbabwe. Ore bodies typically contain 3 – 5 g/ton PGMs, and mined ore needs to be concentrated through mineral processing. The ore is crushed and milled to liberate relevant metals in the ore rock. Flootation is used to separate the PGMs and base metals associated with sulphides from the gangue material.

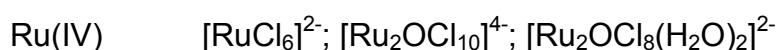
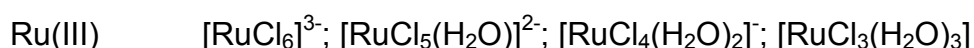
The concentrate thus produced is smelted and converted in electric arc furnaces to produce a base metal sulphide matte and PGM-Ni alloy phase. The matte undergoes crushing and magnetic separation to separate the base metals from the PGM alloys. This PGM concentrate (known as final concentrate, FICO) is then leached in HCl aqueous solution in the presence of  $\text{Cl}_2$ . The different PGM metals are then separated from each other mainly by ion exchange or solvent extraction. This separation is achieved through manipulation of the different oxidation states of all the metals. Ion exchange and solvent extraction are ideal as these processes ensure high selectivity. Once separated, the different metals are then purified and reduced. The refining process of PGMs has not changed significantly over the last few years and the basic principles remain the same.

The process for separating Ru from the other PGMs is similar across most refineries throughout the world, where the volatile state of Ru is used. In INCO's action refinery sodium bisulphate fusion separates the insoluble Rh from Ir and Ru. Ru is separated from Ir through sodium peroxide fusion. Ru is volatilised to ruthenium tetroxide followed by hydrochloric acid addition to form a ruthenium chloride salt which in turn is reduced (Seddon & Seddon, 1984).

The Anglo Platinum PMR uses similar processes to recover and purify the Ru. These use chemical reduction and oxidation to achieve the different oxidation states of Ru for separation. After separation from the other precious metals a substitution reaction with  $\text{NH}_4\text{Cl}$  precipitate the Ru as  $(\text{NH}_4)_2\text{RuCl}_6$ . The final step reduces the Ru salt to metal in a furnace at 800 °C.

## 2.3 Ruthenium chloride speciation

The PMR and most other refineries make use of mainly chloride to refine the PGMs. The ruthenium chemistry is similar to the chemistry of rhodium and iridium in terms of chloride association. Ruthenium forms strong stable complexes with chloride, of which the Ru(III) oxidation state is the most stable, although Ru(IV) are also stable under certain conditions (Viljoen, 2003). The most common species for Ru in chloride media include (Bernardis, Grant & Sherrington, 2005):



Of all PGM species, ruthenium speciation is the most complex due to the range of oxidation states it can achieve. Ru has eight oxidation states and also forms multinuclear species. The chemistry of the different oxidation states, particularly the lower ones, is not yet fully understood. The available information on Ru speciation in the literature is limited and somewhat contradictory. This is probably because many different phenomena come into play when dealing with ruthenium chemistry, which are sometimes mistakenly simplified. These phenomena include oxidation-reduction, polymerisation and complexation (Bernardis, Grant & Sherrington, 2005) (Rechnitz & Goodkin, 1963).

It is important to understand the different species and also know what the species are that will take part in the ACR precipitation at the specified conditions. These species behave differently at certain parameters and could therefore be limiting the conversion of ACR.

### 2.3.1 *Ru(VIII) and other high oxidation states*

As mentioned already, the Ru(VIII) specie is one of the most distinct species of the PGMs through the fact that  $\text{RuO}_4$  is volatile under normal operating conditions, This is a characteristic that is exploited in the industry as it makes the selective separation from the other PGMs possible. Although  $\text{RuO}_4$  is less toxic than the similar  $\text{OsO}_4$ , it should still be treated as extremely poisonous.

$\text{RuO}_4$  is commonly prepared through oxidising Ru(IV) with chlorine and is in itself an extremely powerful oxidant. It is highly unstable and can selectively be reduced to Ru(IV) by HCl. (Seddon & Seddon, 1984). Another study supporting this, is when  $\text{K}_2[\text{Ru(IV)Cl}_6]$  was obtained by reducing  $\text{RuO}_4$  with HCl and then precipitating with KCl (Pshenitsyn &

Ezerskaya, 1960). It is the latter reduction that is used at the PMR to achieve an aqueous Ru solution with mainly Ru(IV) present (equation 1).

The oxidation states Ru(VI) and Ru(VII) exist but are unstable and difficult to isolate in a chloride medium.

### 2.3.2 Monomeric and dimeric Ru(IV) speciation

At PMR conditions, the Ru(IV) species is the most favoured. The aqueous Ru(IV) chemistry is complex, which can be mainly attributed to three different types of reactions taking place: monomeric and dimeric species, aquation reactions and the reduction to Ru(III) (Seddon & Seddon, 1984).

The main Ru(IV) species present at high chloride and acid concentrations is the monomer,  $[\text{Ru}(\text{IV})\text{Cl}_6]^{2-}$ . However, at an increased Ru concentration it becomes evident that a dimerisation reaction takes place, and a dimer species,  $[\text{Ru}_2\text{OCl}_{10}]^{4-}$ , is formed. The commonly accepted reaction equation for this dimerisation reaction is given in equation 3.

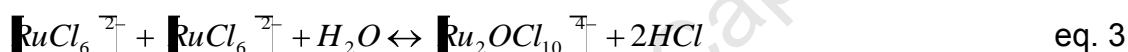


Table 1 reflects the ratio of monomer to dimer at different Ru concentrations in a 6 M HCl solution at ambient conditions (Grant, 1998):

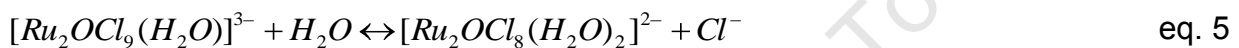
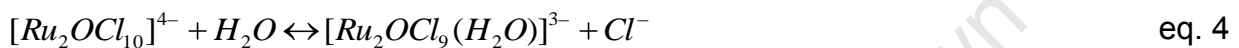
**Table 1: Monomer-Dimer Ru(IV) ratios at different Ru concentrations**

Ru concentration(g/l)	Ratio $[\text{RuCl}_6]^{2-}:[\text{Ru}_2\text{OCl}_{10}]^{4-}$
2	16.2:1
5	1.63:1
10	0.56:1

Pshenitsyn & Ezerskaya (1960) confirmed the presence of an impurity of  $\text{K}_4[\text{Ru}_2(\text{IV})\text{OCl}_{10}]$  when  $\text{K}_2[\text{Ru}(\text{IV})\text{Cl}_6]$  was obtained through reduction of  $\text{RuO}_4$  with HCl and then precipitation with KCl. The authors also showed that pure  $\text{K}_2[\text{Ru}(\text{IV})\text{Cl}_6]$  can be prepared without  $[\text{Ru}_2(\text{IV})\text{OCl}_{10}]^{4-}$  impurity, but only at low concentrations of the initial salt. The stability of  $[\text{Ru}(\text{IV})\text{Cl}_6]^{2-}$  increases in the presence of high concentrations of  $\text{Cl}^-$  and increases at low concentrations of Ru.

By reduction of  $K_4[Ru_2OCl_{10}]$  in ethanol and then re-oxidising to  $K_2[RuCl_6]$  in chlorine one can increase the purity of hexachlororuthenate. This can also be achieved by oxidising  $K_4[Ru_2OCl_{10}]$  with hydrogen peroxide in a 1 M HCl solution and then reducing the product with an equal amount of concentrated HCl solution (Seddon & Seddon, 1984).

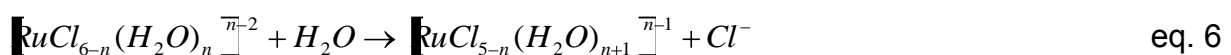
Rard (1984) showed that the hydrolysis of  $[Ru_2OCl_{10}]^{4-}$  causes  $[Ru_2OCl_{10}]^{4-}$  to disassociate, which in turn causes the dimer to depolymerise. This de-polymerisation will be more evident in lower concentrations of HCl. Equation 4 holds true if the HCl concentration is between 6 M and 10 M. Similarly if the HCl concentration is between 3 M and 0.5M equation 5 will hold. These models only hold if the  $Cl^-$  concentration is over 500 times that of the Ru concentration.



Therefore it is evident that, at PMR's operating conditions (6 M HCl and 50 g/l Ru (IV)) the dominant species present will be that of the dimer,  $[Ru_2OCl_{10}]^{4-}$ , but that at lower concentrations the monomer Ru(IV) specie will become more dominant. Therefore, at the start of the precipitation of ACR mostly  $[Ru_2OCl_{10}]^{4-}$  will be present, but as the concentration decreases, the  $[RuCl_6]^{2-}$  will become dominant.

### 2.3.3 Aquation of Ru(IV) species

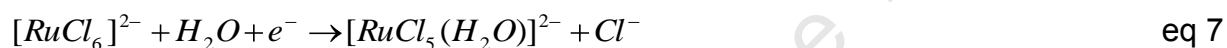
At high chloride concentrations  $[Ru(IV)Cl_6]^{2-}$  is the most dominant specie, however, as the chloride concentration decreases, the complex will undergo aquation reactions. During aquation, a  $Cl^-$  ligand is replaced with a water molecule. The general reaction model that is followed during aquation is seen in equation 6 (Viljoen, 2003). Unlike the other PGMs, aquation of the Ru(IV) specie can occur even in strong chloride media (Grant, 1998). Standing solutions of  $K_2[RuCl_6]$  in water are slowly converted to aqua chloro-complexes.



In light of all mentioned above, it is unlikely but possible that Ru(IV) aquated species will be present in the solution prior to and post ACR precipitation. Given longer reaction time, more aquation can take place, especially at lower  $Cl^-$  concentrations.

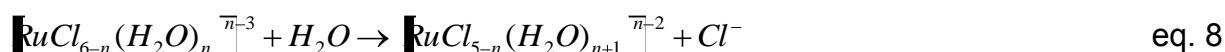
### 2.3.4 Ru(IV) conversion to Ru(III) species

The Ru(III) oxidation state is the most stable oxidation state of ruthenium. Ru(IV) is only stable at specific conditions. A study done by Pshenitsyn and Ezerskaya (1960) described analytical methods for preparing  $[\text{Ru(IV)Cl}_6]^{2-}$  from  $[\text{Ru}_2(\text{IV})\text{OCl}_{10}]^{4-}$  and  $[\text{Ru(III)Cl}_5\text{H}_2\text{O}]^{2-}$ . This study was done at various acidic concentrations in the presence of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). It was found that at very high acidic conditions and high Ru concentrations the  $\text{K}_4[\text{Ru}_2(\text{IV})\text{OCl}_{10}]$  product was favourable and at 6 M acid neither  $[\text{Ru(III)Cl}_5\text{H}_2\text{O}]^{2-}$  nor  $[\text{Ru(IV)Cl}_6]^{2-}$  was present. However partial reduction of  $[\text{Ru(IV)Cl}_6]^{2-}$  occurs if the complex is left with 6 M acid for long periods of time, during which  $[\text{Ru(III)Cl}_5\text{H}_2\text{O}]^{2-}$  forms (equation 7). This reduction to Ru(III) becomes evident especially at higher temperatures (40°C and above). The reduction most probably occurs through oxidation of  $\text{Cl}^-$  to  $\text{Cl}_2$  gas. However the stability of the  $[\text{Ru(IV)Cl}_6]^{2-}$  increases at higher chloride concentrations and in the presence of an oxidant.



Viljoen (2003) and Grant (1988) also claim that Ru(IV) is reduced to  $[\text{Ru(III)Cl}_5\text{H}_2\text{O}]^{2-}$  when a chloride solution of  $[\text{Ru(IV)Cl}_6]^{2-}$  is diluted with water (equation 7). Furthermore the  $[\text{RuCl}_5\text{H}_2\text{O}]^{2-}$  complex will in turn then form  $[\text{Ru(III)Cl}_6]^{3-}$  at higher chloride concentrations (Taqui Kan et al., 1988).

Similar to Ru(IV), aquation on Ru(III) species occur at lower chloride concentration. At 6 M the species  $[\text{Ru(III)Cl}_5\text{H}_2\text{O}]^{2-}$  is most dominant (Taqui Kan et al, 1988). The aquation of Ru(III) takes place according to equation 8. The complex  $[\text{Ru(III)Cl}_5(\text{H}_2\text{O})]^{2-}$  exist in solutions where the HCl concentrations are above 6 M (Viljoen, 2003). At higher acid concentrations, the specie  $[\text{Ru(III)Cl}_6]^{3-}$  is most dominant. A  $\text{Cl}^-$  can be replaced by a water to form  $[\text{RuCl}_5\text{H}_2\text{O}]^{2-}$  (equation 8 where  $n = 0$ ). This substitution happens relatively fast while further aquation is much slower (Cotton & Wilkinson, 1972).



There is a possibility of Ru(III) species being present with the Ru(IV) dimer and monomer at the stated acid, Ru and chloride concentrations. The feed entering the side stream prior to boiling (at 3.5 M HCl) could contain Ru(III) and associated aquated Ru(III) species. Upon boiling the liquor, more Ru(III) can form due to higher temperatures as per equation

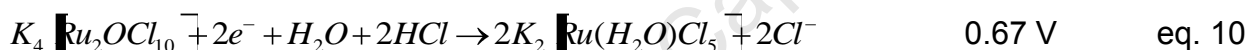
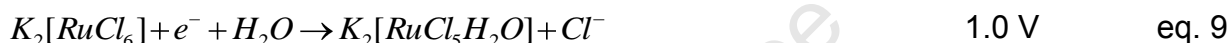
7. The longer the liquor boils, the more reaction time is available for the reduction to Ru(III). If any Ru(III) species form, it will most likely be  $[\text{RuCl}_5\text{H}_2\text{O}]^{2-}$ .

If the said Ru(III) specie is present, it is possible to convert this back to the Ru(IV) monomer or dimer species in the presence of  $\text{H}_2\text{O}_2$  at high HCl concentrations.

### 2.3.5 Redox potential of Ru(IV) and Ru(III)

The above redox reactions should occur at a specific measurable redox potential. This will indicate whether it is thermodynamically possible for the reduction/oxidation to occur.

Various studies were done in order to determine the redox potentials for the redox pair Ru(IV) and Ru(III). These studies showed contradictory results. Values reported by Psenitsyn and Ezeiskaya gave the following potentials (equations 9 and 10) relative to the normal hydrogen electrode (NHE) (Rechnitz & Goodkin, 1963) (Pshenitsyn & Ezerskaya, 1960)



The redox potential of the reaction given in equation 9 above is given as 0.83 V by Grant with Ru (IV) being the most stable oxidation state (Bernardis, Grant & Sherrington, 2005). This difference could either be due to the lack of rapid, reversible reactions or it can be due to the inaccuracy of the measurement used at such high potentials.

### 2.3.6 Colours of precipitate for various Ru species

Different colours are associated with the various oxidation states of Ru. Ru(IV) gives a dark brown to black colour while both  $[\text{NH}_4]_3[\text{RuCl}_6] \cdot \text{H}_2\text{O}$  and  $[\text{NH}_4]_2[\text{RuCl}_5(\text{H}_2\text{O})]$  form a red crystalline product. Ru(II) has a blue colour and its salts are therefore known as the ruthenium blues. Hexaamineruthenium(III) salts are colourless or yellow and water soluble (Seddon & Seddon, 1984). Table 2 summarises the precipitate colour and solubility of the main species discussed above:

**Table 2: Colour and solubility of Ru-chloro complexes**

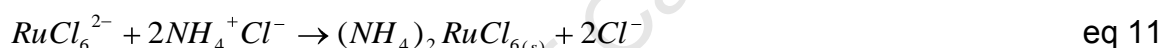
Compound	Colour and solid structure	Solubility
$(\text{NH}_4)_2[\text{RuCl}_6]$	Black crystal	Water & acid

$K_2RuCl_6$	Black crystal	Water & acid
$K_4[Ru_2OCl_{10}]H_2O$	Dark brown crystal	Water
$K_2[RuH_2OCl_5]$	Dark red crystal	Water & acid
$K_3[RuCl_6]$	Dark red powder	Water & acid
$RuCl_3$	Brown powder or Black crystal	-

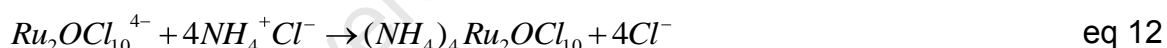
### 2.3.7 Ammonium chloride

PGMs form hexachloro-complex anions predominantly at high chloride concentrations. These ions are then precipitated with  $NH_4Cl$  to purify the metals. An ammonia Ru salt is easily reduced to pure metal by applying heat, which therefore makes for easy, clean processing. Historically, refineries have been using this process from the 1970s to this day. (Bernardis, Grant & Sherrington, 2005) (Precious metals refinery, 2010).

The reaction path that the Ru(IV) follows at high chloride concentrations with ammonium chloride in a hydrochloric acidic medium is believed to proceed according to equation 11:



The dimer specie as discussed above can also be precipitated with  $NH_4Cl$ . The precipitation of this dimer specie follows the following mechanism (equation 12):



The ruthenium trivalent species form a much more soluble ammonia salt compared to the tetravalent hexachloro specie (Bernardis, Grant & Sherrington, 2005). Therefore, if more  $[RuCl_5H_2O]^{2-}$  is formed, the yield will decrease because more of the Ru will stay in solution.

Unfortunately no concrete data could be found for the solubility of either the trivalent or tetravalent ammonium salts in the literature searched. Due to the lack of this data an investigation of the solubility will be included in the study.

## 2.4 Industrial process studies

The PMR was designed and built according to the SAREF (South Africa Refineries) design and the plant was commissioned in 1989. The process for recovery and purification of Ru has not changed significantly from the process used in the SAREF design. The changes

that were implemented were as a result of studies done on operational issues experienced through the years. The process mentioned earlier in this document is the currently applied process and the changes implemented ever since the SAREF design will be listed below. This list is restricted to changes relevant to the ACR precipitation step only.

#### **2.4.1 Exclusion of “Os removal stage”**

A change recently implemented was to exclude the “Os removal stage” from the flow sheet. The main purpose of this step was to remove any Os present in the feed liquor. The Os is co-extracted with Ru, as both are volatile and scrubbed with HCl acid. Any Os present will precipitate with the Ru and eventually report to the Ru metal as impurity. The Os removal step involved the addition of hydrogen peroxide to the feed liquor and subsequent boiling under reflux conditions for 2 hrs.

In earlier years, the Os recovery in the upstream processes of PMR was not efficient, resulting in Os reporting to the final Ru metal. Optimisation work was done to recover most of the Os at the very beginning of the PMR flow sheet, resulting in limited amounts of Os reporting to the Ru side stream. This gave rise to an investigation into the yield of the ACR precipitation step upon removal of the Os removal stage. The addition of hydrogen peroxide and the boiling of the liquor for 2 hours at reflux were discontinued.

Discontinuing the Os removal stage resulted in a noticeable improvement on the yield of Ru during the ACR precipitation reaction. Discontinuing the Os removal stage did not show any effect on the concentration of Os before or after the ACR precipitation reaction. These findings concluded that the “Os removal stage” did not significantly remove the Os when the Os enters the feed solution at low concentrations (< 1 000 ppm) (Hagemann, 2007).

However, the reasons for the improvement in Ru yield were not determined. The yield could have improved due to the elimination of the two hours boiling time under reflux. This supports the hypothesis that Ru(III) species form at high temperatures over time. The removal of this stage in effect caused less  $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$  to form and therefore an increase in yield because of the higher solubility of  $(\text{NH}_4)_2[\text{RuCl}_5\text{H}_2\text{O}]$ .

Upon discontinuing the Os removal stage the addition of  $\text{H}_2\text{O}_2$  was also discontinued. The effect of the  $\text{H}_2\text{O}_2$  on the Ru did not form part of the investigation by Hagemann (2007) and therefore this aspect should also form part of the scope of the current investigation.

### **2.4.2 Shorter boil-down**

The Ru feed liquor is boiled initially to increase the Ru concentration. Engelbrecht & Phage (2008) did an investigation aiming to determine if longer boil-down times do result in a lower yield. The study approached the objective from two sides. Firstly was to establish if there was any statistical difference when operational data was compared. Data for batches that had long boil-down times were compared to batches with shorter boil-down times, the data showed statistically the longer boil-down times resulted in lower yields. Secondly, experiments were done on a laboratory scale. The results of two cases were compared to each other. In the first case the temperature at which the liquor was evaporated was 98°C, and for the second case the liquor was evaporated at 60°C. The experimental results were inconclusive and revealed that there was no difference. The study was only preliminary and it was recommended that further, more extensive work should be done. The evaporation done at 60°C is questionable as higher temperatures promote other reactions and it is important to do the evaporation at the same temperatures to allow proper comparison.

### **2.4.3 Study on the increase of particle size of ACR**

A major operational constraint on the ACR precipitation process at the PMR was the excessive filtration times experienced. This filtration step could sometimes take as much as 24 hours to filter a 20 kg Ru batch. A study was done in conjunction with Anglo Research (AR) to improve the particle size, subsequently decreasing filtration times. The following conclusions were reached (Brits, Khumwenda & Hagemann, 2001):

- Precipitation at reflux (boiling temperatures) produced high moisture content, while precipitation at 80°C and 95°C produced half the moisture content.
- Chilling the slurry to below 5°C offers no real advantage as the yield only improved marginally while the moisture content increased slightly.
- Decreasing the starting Ru concentration of 250 g/l to 50 g/l yielded the best crystal size.
- A stoichiometric excess  $\text{NH}_4\text{Cl}$  to ruthenium ratio of 140 – 174 %, and a reagent addition time of 7.5 l/min yielded best results in terms of recovery and particle size.

## 2.5 Precipitation

The term “precipitation” is generally used for the formation of compounds that have very low solubility. Therefore the formation of  $(\text{NH}_4)\text{RuCl}_6$  is a typical precipitation reaction. It will follow the general principles of precipitation, and any variables that influence precipitation reactions in general will be applicable to precipitating ACR.

### 2.5.1 Supersaturation

Any compound can only be precipitated if the host solution is super-saturated by this compound. Supersaturation is the term used for the relative concentration of a compound at a certain point in time above the solubility of that compound at a specific condition (Lewis, 2008). This supersaturation of the compounds could be instantly achieved by mixing two reactants or by cooling. Because precipitation occurs at the point of supersaturation, the precipitation proceeds rapidly and causes fine nuclei to form (Giulietti, Seckler & Derenzo, 2001). In order to avoid handling and filtering of difficult colloidal particles, the precipitation should be done at lower supersaturation. Controlling supersaturation is the key to controlling precipitation reactions (Lewis, 2008).

The crystalline product and the crystal size are mainly dependent on the precipitation kinetics and therefore the degree of supersaturation. In order to get a uniform crystal size, it is crucial to maintain the optimum supersaturation in all locations within the reaction vessel. When dealing with sparingly soluble systems the following factors are important to ensure a uniform and optimum degree of supersaturation (Mersmann, 1999):

- Concentration of the reactants – for a coarse product low concentrations (diluted) are needed, however the more diluted the reagents the lower the degree of supersaturation and hence the lower the yield of precipitation;
- Products having a high concentration but low solubility will increase yield;
- Rate of the chemical reaction – a slower reagent addition could form smaller particles because it will control the degree of supersaturation (Hagemann, 2003);
- Rapid mixing for fast chemical reaction causes the chemicals to be more distributed and a more uniform product size will be formed;
- Good macro mixing for coarse products can also be achieved through simultaneous addition of reagents (Hagemann, 2003);
- Seeding could aid in a coarse product;

- Agglomeration;
- Temperature - The largest particles result at temperatures just below boiling point. The reason for this is that equilibrium solubility is dependant on temperature and at higher temperatures the equilibrium solubility is usually higher. This decreases supersaturation and subsequently particle size (Hagemann, 2003). The rate of reaction can also be affected by temperature for precipitation reactions that are kinetically rate limited.

For compounds that are very soluble, supersaturation is achieved by cooling or evaporating, while slightly soluble compounds are supersaturated by means of chemical reaction. For both, soluble and less soluble compounds, supersaturation can be generated by the addition of another solvent in which the solute is less soluble (Giulietti, Seckler & Derenzo, 2001).

Chemistry can dominate in precipitation processes where ions interact to form complexes in solution which subsequently precipitate out because of their limited solubility in the solute.

In practice, the same degree of supersaturation in a reactor is not always possible as the reagents do not present the same stoichiometric ratio everywhere within the reactor. It is most supersaturated at the point where the reagent is dispersed into the reactor. The supersaturation is dependant on the distance from the reagent addition point to the mixing zone. The different levels of supersaturation cause uncontrolled formation of solids, and in turn the characteristics of the solids created are influenced. Therefore in any precipitation reactor or vessel the primary focus should be to maintain optimal and uniform supersaturation. Experimental work showed that continuous precipitating processes have bigger particles compared to batch processes because it is difficult to control a uniform supersaturation in a batch process (Mersmann, 1990) (Gosele & Kind, 1991)

### **2.5.2 Ageing & Crystal growth**

Ageing is the term used for exposing the precipitate to the solution for extended periods with the idea of forming bigger particles or improving yield. The ageing period could be days or even months and the stability of the precipitate is governed by the arrangement of molecules within the crystalline structure. Solubility of a compound is linked to the surface area of the crystal structure and small particles tend to have a higher solubility. This effect

is apparent in the later stages of batch precipitation when the supersaturation has decreased and then the smaller particles tend to re-dissolve.

The crystal size could grow due to irregular crystal surfaces or mainly agglomeration. Agglomeration is the transport and collision of particles to one another and is often desired because it leads to larger particles. Mixing intensity improves the particles collision frequency but could also break up the particles if the mixing is too intense. Other factors possibly influencing agglomeration are solid concentration, pH, ionic strength and supersaturation (Giulietti, Seckler & Derenzo, 2001).

As mentioned already the degree of supersaturation is dependant on the distance from the reagent addition point to the mixing zone. This results in heterogeneous primary nucleation and uneven crystal surfaces are formed (Giulietti, Seckler & Derenzo, 2001). Nucleation sites also affect crystal size and the fewer nucleation sites there are, the bigger the crystal size.

Particle growth is not affected by the stirrer speed or the stirrer type as long as all the particles are kept in suspension within the reactor (Sathyamoorthy et.al. 2000). However stirrer speed and type does influence the degree of macromixing and in turn affects the degree of supersaturation and therefore the size of the particles. Another factor to consider is that there is a point where over-stirring within the reactor cause disturbances which can break up the crystals and form more nucleation sites (Boyle, 2006).

Based on the information it is unlikely that ageing will be beneficial for ACR precipitation. The particles formed during the ACR precipitation will be mostly dominated by the reaction. However it is important to keep all considerations in mind when setting up the experiments. The type of agitator and speed should be set so that all particles are kept in suspension.

### **2.5.3 *Mixing***

Large crystals should be produced at low supersaturation and the reactants should be added near areas of high mixing intensity and as far away from each other as possible. Three different types of mixing occur in a precipitation process and usually one of these mixing types determines the type of precipitate that is formed because it determines the supersaturation occurring in the process. These mixing types are: macro, meso and micro mixing and different correlations for determining these mixing times are available in

the literature. Macro mixing is mainly determined by the mechanics of the reactor for example stirrer speed. Meso mixing is dependant on the flow rate at the inlet of the reactants. Micro mixing is determined on the homogeneity of the mixed solution (Lewis, 2008).

In order to rule out the effects on mixing on the yield and particle size, all experiments should be done at similar mixing conditions.

## **2.6 Inductively coupled plasma arc atomic emission spectroscopy (ICP-AES)**

Quantification of the experimental result is of great importance to test the various hypotheses. The Ru element has to be individually and quantitatively measured in the feed sample and filtrate sample in order to determine yield. At the PMR refinery the method that has been developed and is used on a daily basis is the inductively coupled plasma arc (ICP) spectroscopy.

Atomization is the term used for converting elements in a sample to gaseous atoms or elementary ions. Optical atomic emission spectrometry (AES) is used for qualitative and quantitative elemental analysis. Components of samples are converted to atoms (or elementary ions) and these species are excited to a higher electronic-magnetic energy state (electrons in a higher orbital). This excited state is very brief and rapidly returns to the elements basic orbital state. Relaxation of these excited species emits a quantum of energy which gives rise to ultraviolet and visible light spectra. The visible spectrum can be accurately detected if wavelengths are between spectra 120 – 850 nm. Spectra not falling in the range mentioned are not detected accurately. Ru emits at wavelengths between 185 and 400 nm. Plasma energy sources are mostly used in industrial analytical chemistry for the purpose of AES. The main advantages of plasma are the lower inter elemental interference and dozens of elements can be analyzed simultaneously. Argon is used in the plasma as the Ar ions are capable of absorbing sufficient power to maintain temperatures at which the plasma operate (typically 4 000 to 6 000 K). A plasma source does not 'burn' (oxidize) and therefore there is no combustion (Skoog et.al. 1998) (Manning & Grow, 1997).

All metallic elements can be analyzed and some other non-metallic elements. Different lines are emitted for the same element and a suitable line is usually chosen as a standard,

depending on the overlapping of other lines. The specific lines used for Ru are 240.272 nm, 372.610 nm and 245.553 nm. At the PMR the line used that has the least amount of interference is 240.272 nm.

Calibration should be done periodically to account for instrumental drift. Calibration curves are done as a function of the transducer voltage relative to the concentration in the injected solution. This is usually a linear relationship plotted on a logarithmic scale and follows linearity, except for higher concentrations of the sample where the line starts to bend. For this reason good sample preparation is needed and the sample is usually diluted. The detection limit for various components differ and the detection limit for Ru is 6 ppb (Skoog et.al. 1998) (Manning & Grow, 1997).

The width of atomic lines is of great importance in AES. Narrow lines are desirable as they tend to show no interference from overlapping elements. The sample is nebulised and transported to the plasma with a carrier gas (typically Ar) which does not emit light at the measured frequencies.

The plasma produces an oscillating magnetic field which in turn creates an oscillating current on the electrons of the carrier gas (Ar). This energy is transferred between atoms of the Ar gas which causes collisions and creates the high temperatures. The light is emitted by the atoms and is converted into an electrical signal by a photomultiplier (Skoog et.al. 1998) (Manning & Grow, 1997).

## **2.7 Ion exchange chromatography**

As mentioned in the section on speciation (2.3) there is a possibility that not all Ru exists as hexachlororuthenate but as other species. In order to thoroughly test what happens to the speciation when certain parameters are varied, a method for determining speciation is required.

The determination of ionic species is very important in the field of analytical chemistry. Ion chromatography has been studied from as early as 1903 where leaf pigments were separated on a polar solid phase. Ion exchange chromatography offers several advantages above other analytical methods (Weiss, 2004) (Bassett et.al. 1989). Advantages include:

- Speed – fast analysis with an average time of 10 min per sample;

- Sensitivity – detect ions at very low concentrations;
- Selectivity – distinguished between different ions easily if the right method is chosen;
- Simultaneous detection – detect different ions in the same sample;
- Stability of the separator columns – very stable and versatile packing material is available for all different kinds of organic and inorganic ions;
- Repetitive and reproducible analysis using the same column.

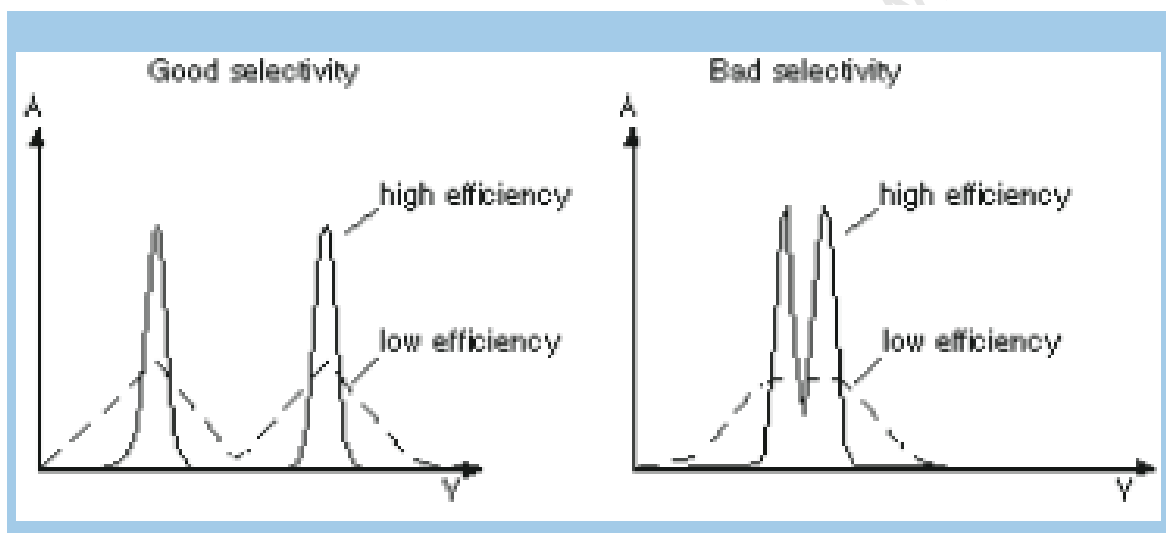
Ion exchange chromatography (IC) is classified under liquid chromatography and concerns the separation of ionic mixtures. Separation in ion exchange chromatography is achieved through reversible adsorption/desorption of specific ions on the column resin. Two different functional groups are used, a cation and anion resin. An acidic functional group releases a positively charged  $H^+$ -ion and attracts a cation to its negative site. Similarly a base ion group attracts an anion to its positive site. Because there are differences in equilibrium quotients of the different ions, the different ions will exchange sites for a length of time and will then be released at different times causing the separation of ions (Shugar & Ballinger, 1996).

Separation of the different ions in a solution is possible due to the difference in ion charge, charge densities and charge distribution on their surfaces. The separation of the ions happens usually in four to five stages (Amersham Biosciences):

- Stage 1 – Before a sample or eluant is introduced to the column, all ions are in equilibrium and the ion exchange resin is at a particular pH and ionic strength.
- Stage 2 – A sample is injected into the column and the solute ions displace the counter-ions of the ion-exchanger through adsorption, thereby binding to the gel.
- Stage 3 – Substances are removed from the column by desorption, whereby an eluant is passed through the column. The eluant has a different ionic strength or a different pH. The ions in the eluant replace the sampled ions from the resin which results in the sampled ions exiting the column with the eluant. Different molecules are removed in order of their binding strength, generally the more weakly bound ions first. The eluant effectively “pushes” the ions out of the column and operates similar to a packed bed reactor.
- Stage 4 – Removal of all substances from the column and re-charging the gel.

The fundamental part of an ion exchanger is the presence of a particular charge group. This charge group determines whether it is a cation or anion type or a weak or strong ion exchanger. A strong ion exchanger does not refer to the strength of binding but to the flexibility of the ion-exchanger that can operate over a wide pH range.

Two main parameters affecting the efficiency of columns are the bead size and the correct packing of the bed. The selectivity however is as an important parameter as the efficiency and the selectivity is determined by the type of ion-exchanger and the conditions such as pH and ionic strength. Figure 3 shows the difference between selectivity and efficiency. The capacity of an ion exchanger column is a quantitative measure of the ability to take up counter ions. The ionic capacity is the number of charged groups per mass of the exchanger (Amersham)



**Figure 3: Ion-exchange chromatography selectivity and efficiency (Amersham)**

Higher charged (polyvalent) ionic species are retained more strongly in the solid phase than singularly charged ions. For a specific charged group, differences in the size of the hydrated ions also have an effect where the larger ions tend to be retained on the solid phase (Skoog et.al. 1998). Therefore the polyvalent charged ions that are large will exit the column last. Anion chromatographic separation of metal chloride complexes follows in the order  $[MCl_6]^{2-} > [MCl_4]^{2-} > [MCl_6]^{3-} >$  aquospecies (Jones & Schwedt, 1998). This is specifically applicable to the species present in the Ru liquor. The Ru(IV) monomer specie will therefore exit before the Ru(III) specie and the Ru(IV) dimer specie will be retained the longest.

Standard columns are designed for specific separations. Dionex offers a large number of columns and more specifically for this study, the IonPac® AS11HC columns. These columns are specifically designed for organic and inorganic anion separation. This is a high capacity column that allows more concentrated samples without overloading the column and less peak broadening (peak broadening occurs when the different species are not selectively separated and the peaks overshadow each other which causes one broad peak). The functional group is an alkanol quaternary ammonium, and the average adsorbent bead diameter is 9 µm. The eluant must be stored under a helium atmosphere to ensure contamination free operation and proper pump performance. 10 µL is used for sample volume. A clean up solution is specified as 1 – 3 M HCl. (Dionex, 2008)

In order to quantify the species present the eluant solution should be analysed. Various analytical methods can be used. If an ICP is used the peaks are measured through intensity as described in the previous section. The different species will have different intensity peaks. The area (time vs. intensity) of the peak can be determined. The ratio of the different peaks can then be measured relative to each other (Bassett, et.al. 1998).

One of the disadvantages of IC is that there could be excess reagent and by-products present which can interfere with the separation (Bassett, et.al. 1998).

## 3 EXPERIMENTAL METHOD

### 3.1 Experimental methodology

Experiments were conducted in order to test the hypotheses. The experimental set-up aimed at keeping all experimental parameters similar and only the applicable parameters testing the relevant hypothesis were changed. The hypotheses are formulated from the literature and previous investigations. Statistics will be used to determine if the experimental results are significant. The t-test will be used with a 95 % confidence level. (Weiers, 2008). From the results obtained and the review literature various deductions will be made. These conclusions should state if the hypothesis was proved or not.

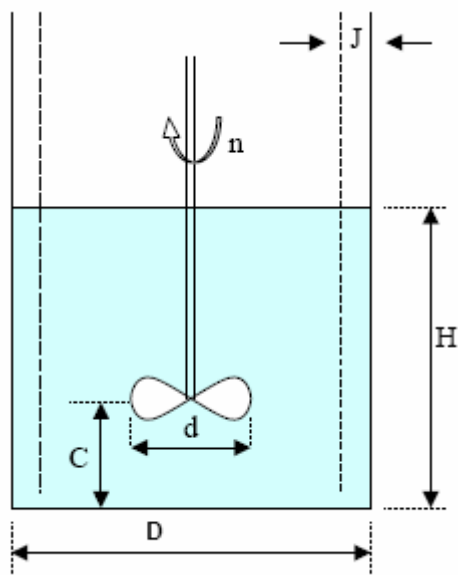
### 3.2 Experimental setup

#### 3.2.1 Equipment

The liquor treated has a concentration of 6 M hydrochloric acid and is highly corrosive, therefore all equipment was made of glass or a suitable acid resistant material. The current operation at the PMR uses batch processing for this specific precipitation step. Similarly, a batch glass reactor was designed specifically to accommodate precipitation reactions.

The dimensions of a reactor are of great importance when precipitation occurs as it influences macro mixing. It is also important to keep all particles in suspension throughout the experiment, but the contents should not be stirred too vigorously as this can also break up particles. Although mixing has a direct impact on the particle size and degree of supersaturation, all experiments have been conducted using the same degree of mixing and are therefore directly comparable. Figure 4 and the equations following (equation 13 to 16) are typically used for precipitation reactions. Table 3 lists the dimensions of the specific reactor used during the experiments.

Three baffles and an overhead 4 blade axial stirrer were used to ensure that proper mixing and solid suspension takes place. The overhead stirrer was set at 350 - 370 rpm. A glass condenser with cooling water was used to ensure refluxing conditions during the experiment. The refluxing conditions ensure that minimum vapour is lost to the atmosphere.



**Figure 4: Reactor dimensions specifically for precipitation reactions**

$$\frac{d}{D} = 0.33 \quad \text{eq. 13}$$

$$\frac{c}{D} = 0.3 \quad \text{eq. 14}$$

$$\frac{H}{D} \sim 1(0.8-1.2) \quad \text{eq. 15}$$

$$J/D = 0.1 \quad \text{eq. 16}$$

**Table 3: Dimensions of reactor used during experimental work**

Variable	Reactor dimensions
D, Vessel inside diameter(mm)	125
V, Total volume of reactor (L)*	1.6
n, stirrer speed (rpm)	350 – 370
D, stirrer diameter (mm)	42
C, stirrer from bottom (mm)	~ 30
H, Height of liquor (mm)	60 – 125
J, baffle width (mm)	12.5

\* Maximum volume of reactor

The temperature was controlled by a temperature controller and hotplate. The  $\text{NH}_4\text{Cl}$  was added with the use of a peristaltic dosing pump at a rate of 7.5 ml/min. The point of  $\text{NH}_4\text{Cl}$

addition took place on the surface of the liquor. At the end of the run the contents was shock-cooled to below 40°C by placing the hot reactor and its contents in a bath filled with cold water (< 20 °C) The contents were then filtered on a Millipore™ apparatus using a filter media of 0.45 µm. No solids bypassed the filter media.

### **3.2.2 Experimental liquor**

Experimental batches of 1 litre were used in all experiments to ensure consistency. For each specific variable tested the same batch liquor was used to limit the amount of variability in the starting liquor. The feed liquor was obtained directly from a production run from the RuO<sub>4</sub> scrubber using 6 M HCl in the PMR.

Five different parameters were varied to test the five different hypotheses. These variables will be explained in more detail in the next section. A batch sample was used to do a base case experiment as well as one experiment for each of the five different variables tested. The same experiments were then repeated 3 times using three different samples. This then required 4 different sample batches, which, for the remainder of this report, will be called batch A, B, C and D. This was specifically done to ensure that fresh feed is used to eliminate any additional variability that could come into play if the feed was standing for a long period. On two of the experimental runs where hydrogen peroxide was tested, a separate base case and batch were used. 35 % H<sub>2</sub>O<sub>2</sub> was used in these experiments.

The concentrated NH<sub>4</sub>Cl solution was prepared in advance. 250 g NH<sub>4</sub>Cl was added to 500 ml of demineralised water. More demineralised water was then added to achieve the one liter mark. It was stirred until all NH<sub>4</sub>Cl was dissolved. The net result was a concentration of 250 g/l NH<sub>4</sub>Cl solution. The saturation limit of NH<sub>4</sub>Cl is 372 g/l at 20 °C (Perry, 1998) but due to operational difficulties a solution of only 250 g/l is used at the PMR to accommodate the colder winter temperatures.

### **3.3 Matrix of experimental parameters**

The experiments were structured in such a way as to test the hypotheses stated. The base case parameters were used in all experiments with the exception of the particular variable that was tested in a specific run. With the testing of each hypothesis only one variable was changed from the base case. The order of the experiments was also randomly varied to eliminate a potential bias that might occur from doing the experiments

in the same order for each batch sample. Below are all the different hypotheses that were tested.

### **3.3.1 Base case**

A base case experiment was done for all sample batches A through D. The different steps of each base case will be outlined stepwise. The exact same procedure was followed for all variables.

- i. An initial head sample was taken for each sample batch and the analytical concentration of Ru was obtained through ICP analysis (section 3.4.1).
- ii. The Ru concentration had to be increased by reducing the volume of the sample. The volume to which the liquor had to be boiled down to obtain a Ru concentration of 50 g /l was calculated from the head sample and initial volume. This volume was measured in the reactor and a mark was made.
- iii. An experimental volume of 1 litre was then added to the reactor and the solution was placed on a heat plate at maximum heat. The concentration for each of the different base cases ranged from 26 g/l to 31 g/l. The liquor boiled at 98°C, and at the start of boil down mostly water evaporated but through boiling the concentration of HCl increased until the azeotrope (~ 6M) of HCl was reached. Therefore at the end of the boil down the solution had a HCl concentration of 6 M. The reactor was left open at the top in order for the liquor to be evaporated with the least amount of condensation.
- iv. Once close to the marked volume, the reactor was removed from the heat source, placed on a flat surface and compared to the mark. This was done for the purpose of accuracy as the bubbles formed by boiling interfered with the reading. Once the liquor was removed from the heat source the bubbles disappeared within a couple of seconds, and therefore this didn't interfere with the experiment. If more boiling was required the solution was returned to the heat source. Once this calculated volume was reached the reactor lid was placed on top and the condenser was put in place. The time it took (which was directly depended on the initial head concentration) was approximately an hour and a half.
- v. A 10 ml sample was taken from the boiled liquor. ICP analysis was done to determine if 50 g/l was achieved. These results were not used to determine the

endpoint of the boiling step since the analysis took too long, making it impractical. The results were used to check if the concentration was 50 g/l. If it wasn't in close proximity the specific run was repeated.

- vi. While the solution was kept under reflux and agitated, the heat was turned off until the solution had cooled to 80°C. This took approximately 10 minutes.
- vii. Based on the mass of Ru in the reactor, a volume of NH<sub>4</sub>Cl was calculated to achieve a stoichiometric excess of 1.5 times. This amounted to approximately 300 ml of NH<sub>4</sub>Cl solution. The NH<sub>4</sub>Cl solution was added at a fixed rate of 7.5 ml/min. The temperature of the NH<sub>4</sub>Cl solution was 25°C and the temperature of the reactor contents was kept constant at 80°C. The agitator was running continuously during reagent addition.
- viii. The addition took approximately 45 min, and once the addition was done a further 15 min reaction time was allowed at 80°C.
- ix. The slurry was then cooled to below 40°C. This was done by placing the reactor in a cooled water bath without the solution being agitated. The total time of cooling was approximately 5 min.
- x. The contents were then filtered on a filter medium of 0.45 µm using vacuum Millipore filtration. No washing was done on the precipitate.
- xi. A sample was taken of the filtrate and the Ru concentration determined by ICP analysis.
- xii. The representative sample of the precipitate was taken and submitted for particle size distribution analysis.

### **3.3.2 Hypothesis 1 – A longer time at boiling point prior to precipitation results in a decrease in yield due to increased dimerisation**

This hypothesis is formulated based on two findings in the literature. The first was the mentioning of the reduction of hexachlororuthenate to pentachlororuthenate as indicated by equation 7. It was mentioned that this conversion can take place just by letting the hexachlororuthenate stand in water and this conversion is promoted at temperatures exceeding 60°C. The pentachlororuthenate also precipitates with ammonium but it has a

higher solubility than that of hexachlororuthenate. The second consideration was the preliminary test work done at the PMR (Engelbrecht & Phage, 2008), which showed that, statistically, the yield of the precipitation reaction decreased with longer boil-down time.

This hypothesis was tested by varying the total time the liquor was boiled. The base case was done as described above in one and a half hours to give a calculated average boil-down rate of 5 ml/min. This test was conducted by boiling the liquor under near reflux conditions for 6 hours. The contents were not under complete reflux and a small outlet was allowed for the some of the vapour to escape the reactor. This resulted in a calculated average boil-down rate of 1.3 ml/min.

### ***3.3.3 Hypothesis 2 – Precipitation at higher temperatures will increase the yield due to faster reaction kinetics***

There is no indication from previous studies whether the extent of this particular reaction is limited by mass transfer or is kinetically rate limited. The reaction kinetics seem fast based on the rate of precipitation when the reagent comes into contact with the ruthenate liquor. However, because of this uncertainty this hypothesis could clarify whether the rate and extent of the reaction could be influenced by the temperature of the reaction. A second part to this particular hypothesis is to increase particle size. It is clearly stated in literature that precipitation done at higher temperatures can have a significant impact on particle size. If it is found that particle size increases significantly then there is the possibility to increase the scope of work as one of the limitations to the work was not to reduce particle size. Other parameters have a greater effect on the degree of supersaturation and produce therefore more nuclei. If the temperature is increased then the net result could possibly lead to an improvement in yield having similar particle size.

The base case addition temperature of the  $\text{NH}_4\text{Cl}$  was done at  $80^\circ\text{C}$ . During this set of experiments the temperature during  $\text{NH}_4\text{Cl}$  addition was  $95^\circ\text{C}$ .

### ***3.3.4 Hypothesis 3 – A higher concentration of boil-down liquor will increase the yield as a higher supersaturation of reagents are present***

All precipitation is driven by supersaturation. If the ruthenate feed liquor is at a higher concentration, then the degree of supersaturation should be increased. This in turn would lead to an increase in yield. Supporting this is the fact that there will be a decrease in the volume at the end of the precipitation with the same amount of Ru present. The Ru

concentration will therefore be higher than the equilibrium solubility concentration and more Ru will be precipitated. Increased supersaturation does however have a direct impact on particle size as it tends to form more nuclei. For this reason only a small increase was made to the initial boil-down concentration. This is to comply with the scope of work which states that the particle size should not decrease.

The boil-down Ru concentration of the base case is 50 g/l and for this hypothesis it is 80 g/l. The volume to achieve this concentration was determined ( $\pm$  300 ml depending on the initial Ru concentration), marked and checked similar to the base case. It took approximately 120 minutes boiling to 80 g/l which is 30 min longer than the boiling time required to boil to 50 g/l.

### **3.3.5 Hypothesis 4 – Increasing the amount of reagent will increase the yield**

The PMR operating conditions add 1.5 times excess  $\text{NH}_4\text{Cl}$  required. This hypothesis is based on two observations from the literature. The first is that at 1.5 times there is not enough reagent to enhance the effect of supersaturation or that the amount of  $\text{NH}_4\text{Cl}$  isn't enough for completing the reaction due to losses of the reagent in possible side reactions. Secondly, adding additional reagent especially when most of the Ru has already been precipitated out, will potentially precipitate more Ru due to creating higher supersaturation. Another possible hypothesis is that it will ensure that none of the Ru that has been precipitated out will dissolve again.

The base line will be done at 1.5 times in excess (~300 ml solution) to that of the stoichiometry while this set of experiments will be done at a stoichiometry of 3 times the required  $\text{NH}_4\text{Cl}$  (~500 ml) needed. The time in which the reagent was added was not varied and therefore the rate of addition was 12 ml/min compared to the base case of 7.5 ml/min. The additional reagent caused considerably more dilution of the Ru in solution. The final solution of the base case amounted to approximately 800 ml compared to the 1 000 ml solution for the runs done with more reagent.

### **3.3.6 Hypothesis 5 – Addition of an oxidant prior to precipitation will increase yield due to the complete conversion of all aquated species to hexachlororuthenate**

The PMR used to add  $\text{H}_2\text{O}_2$  as an oxidant in the Os removal stage following  $\text{RuO}_4$  scrubbing. The main purpose of the  $\text{H}_2\text{O}_2$  was to remove Os from the Ru rich liquor. It was proven that eliminating this 'Os removal' stage improved the yield on the Ru.

However the 'Os removal' stage had two steps of which the first was the addition of H<sub>2</sub>O<sub>2</sub> and the second was boiling under reflux for two hours. It can be argued that the part which improved the yield was the removal of the additional two hours boiling time as described in the first hypothesis. Therefore a clear understanding of what effect H<sub>2</sub>O<sub>2</sub> had on the Ru is required. The literature also suggested that [RuCl<sub>6</sub>]<sup>2-</sup> can be formed by oxidising [Ru(H<sub>2</sub>O)Cl<sub>5</sub>]<sup>2-</sup> in hydrochloric acid in the presence of H<sub>2</sub>O<sub>2</sub>. Therefore the hypothesis is that if H<sub>2</sub>O<sub>2</sub> is added before the boil-down of the feed liquor, any [Ru(H<sub>2</sub>O)Cl<sub>5</sub>]<sup>2-</sup> that might be present will be converted to [RuCl<sub>6</sub>]<sup>2-</sup> and thus precipitated as (NH<sub>4</sub>)<sub>2</sub>RuCl<sub>6</sub>. This will improve the yield as the (NH<sub>4</sub>)<sub>2</sub>RuCl<sub>6</sub> has a lower solubility than (NH<sub>4</sub>)<sub>2</sub>Ru(H<sub>2</sub>O)Cl<sub>5</sub>.

In these experiments, 50 ml H<sub>2</sub>O<sub>2</sub> was added before the boil-down was started. The rest of the experiment was carried out as usual. The concentration of H<sub>2</sub>O<sub>2</sub> used was 30 %.

### 3.3.7 Experimental test matrix

Table 4 list all the parameters that will be varied throughout the investigation. A total of four experiments were done for each of the line items in Table 4. Appendix A list the relevant experimental results for the different experiments conducted.

**Table 4: Varying parameters testing the different hypothesis**

	<i>Boil-down time</i>	<i>Boil-down conc.</i>	<i>Temp. at precip.</i>	<i>Stoich. Excess</i>	<i>H<sub>2</sub>O<sub>2</sub> added</i>
	<i>Min</i>	<i>g/l</i>	<i>g/l</i>	-	<i>ml</i>
Base case	90	50	80	1.5	-
Hypothesis 1	<b>360</b>	50	80	1.5	-
Hypothesis 2	90	50	<b>95</b>	1.5	-
Hypothesis 3	120	<b>80</b>	80	1.5	-
Hypothesis 4	90	50	80	<b>3</b>	-
Hypothesis 5	90	50	80	1.5	<b>50</b>

### 3.3.8 Additional experiments

Some additional experiments were also done to aid in the testing of the hypotheses. These experiments were not repeated unless the results showed potential.

- A similar experiment to the base case was done with the exception that solid  $\text{NH}_4\text{Cl}$  was added to the contents in one slug. The same amount to 1.5 times excess of the required stoichiometry was added.
- An experiment was done where the contents were boiled down to 120 g/l and then 3 times stoichiometric amount of saturated  $\text{NH}_4\text{Cl}$  solution was added.
- Simultaneous addition of  $\text{NH}_4\text{Cl}$  and Ru feed liquor was done. The Ru liquor was evaporated to 50 g/l Ru concentration and during the addition the feed was maintained at  $80^\circ\text{C}$ . Both the reagents were added to a separate reactor simultaneously and the mixed contents were kept at  $80^\circ\text{C}$ . The total addition time for both the reagents was 40 min and the flow rates were adjusted accordingly. The flow rate of the  $\text{NH}_4\text{Cl}$  solution was 7.5 ml/min while the flow rate of the Ru liquor was 12.5 ml/min.
- The solubility of ACR at different HCl and  $\text{NH}_4\text{Cl}$  concentrations were determined experimentally. The different solutions were water, 2 M, 4 M and 6 M HCl and in each of these 0, 1 (20 g/l) and 2 (40 g/l) grams of  $\text{NH}_4\text{Cl}$  was added. These tests were conducted at  $25^\circ\text{C}$ . One test without any  $\text{NH}_4\text{Cl}$  was also done at  $80^\circ\text{C}$  on the different solutes. An amount of 10 g ACR was added to 50 ml of demineralised water and stirred for 2 hours. The slurry was filtered and the Ru concentration was analysed in the filtrate. These results are available in Appendix A.

### 3.4 ANALYSIS

The following analyses were done on the samples:

- Ru concentration for determining the yield- ICP analysis;
- Particle size distribution (PSD) – The particle size was determined by means of a Malvern Mastersizer 2000 Particle Analyser;
- Speciation – Ion-exchange chromatography.

#### 3.4.1 ICP analysis

The ICP was used to determine the Ru concentration and it was used for detecting the Ru species as it exited the column. Because of the change that the calibration curve could have, three dilutions were done on the samples as part of sample preparation. They were 10, 100 and a 1 000 times diluting the initial sample. The 240 nm line typically gave higher results as it is more sensitive and is usually used for low concentrations, while the 372 nm line is used for higher Ru concentrations. However the 240 nm line is a standard across

the Anglo Platinum group and therefore this line was used for all analyses to keep the same basis.

### **3.4.2 Particle size distribution**

All samples were dispersed in ethanol as the ACR is soluble in water and acid. The speed at which the slurry was stirred during measurement, was 1500 rpm.

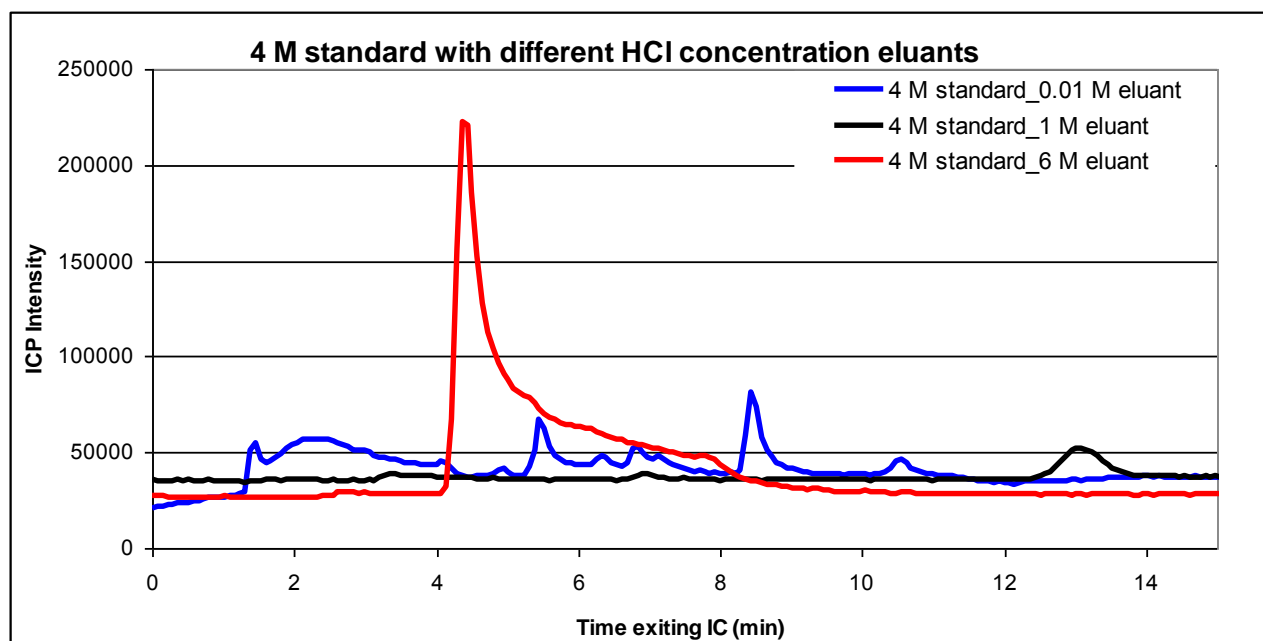
### **3.4.3 Speciation**

As explained in the literature survey, Ru speciation is complex. Speciation was done on specific samples with the main objective to compare the speciation for different experiments whilst varying parameters. A Dionex ion exchange chromatography column was used to separate the different species from each other. The IC was coupled in series to an ICP which showed the intensity of the species as it was exiting the IC

Before speciation was done on the high Ru feed, the samples were diluted 100 fold with 6M HCl. This was done to maintain the selectivity of the separation and to not flood the column. If a column is flooded, not all species are removed and the next run could still release some of the previous samples ions.

Various runs were completed to find the optimum conditions that would give accurate results.

- **Different eluants**

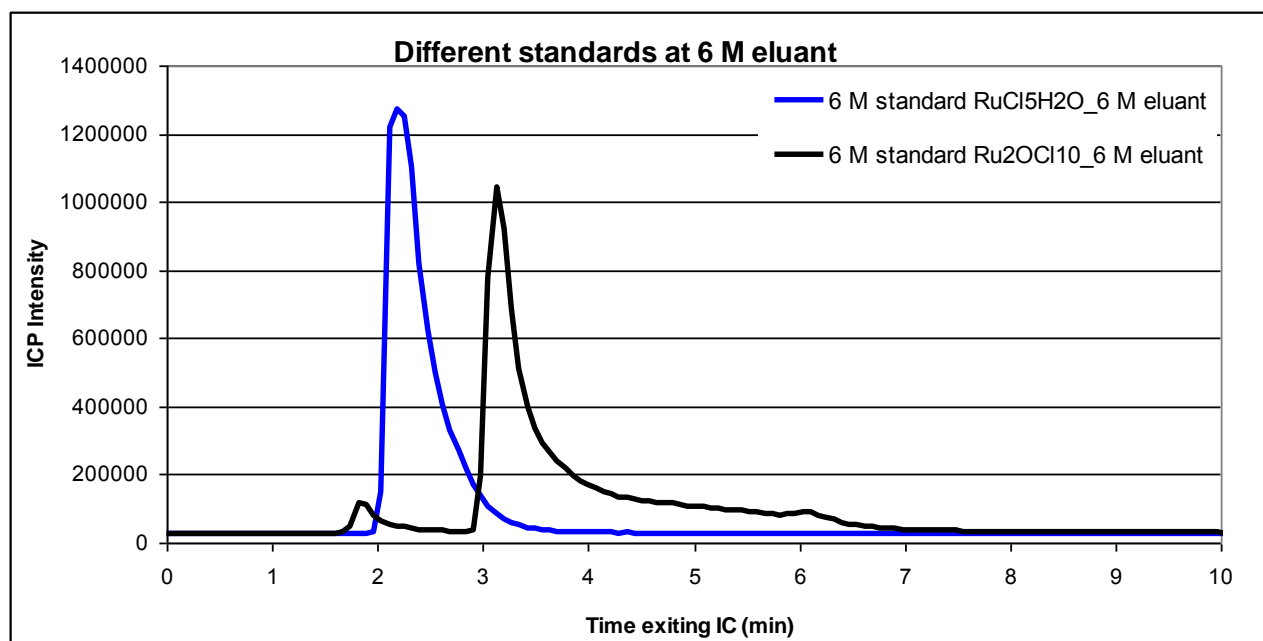


**Figure 5: Speciation diagram – Standard in different HCl concentration eluant**

A sample was prepared from a known salt to obtain a reference profile. This standard profile was then used to compare the other samples. A standard of 1 g/l  $[\text{Ru}_2\text{OCl}_{10}]^{4-}$  was prepared in 4 M HCl. This standard was then run through the IC with 0.01 M, 1 M and 6 M HCl eluant. Figure 5 shows the differences in profiles of the separation of the species. Initially the standard was analysed using a low molarity eluant. The profile using this 0.01M eluant shows many distinctive peaks while the standard at 1 M eluant shows only one distinctive peak. Similarly only one distinctive peak is seen in the profile obtained using the 6 M eluant. The 6 M eluant shows a different peak compared to the 4 M eluant. It is believed that this is the same specie but the higher molarity eluant forces the specie out of the column much faster. This is because there is a higher concentration of  $\text{H}^+$  ions present and therefore a stronger tendency for the anion group to be extracted.

The many peaks resulting from the use of 0.01 M eluant, indicates possible aquation of the Ru species. The aquation takes place due to the lack of  $\text{Cl}^-$  ions present. The  $\text{Cl}^-$  ions are replaced with water molecules as the species move through the column. It was decided to use 6 M HCl as eluant as this will ensure that the species measured are the species present in the particular sample.

- **Different standards**



**Figure 6: Speciation diagram – different standards**

Two standards were prepared in 6 M HCl. A  $[\text{Ru}_2\text{OCl}_{10}]^{4-}$  and  $[\text{RuCl}_5\text{H}_2\text{O}]^{2-}$  standard solution was prepared. The concentration of these standard solutions was 1 g/l and the profiles are displayed in Figure 6. Only one peak is associated with the  $[\text{RuCl}_5\text{H}_2\text{O}]^{2-}$  standard and the  $[\text{Ru}_2\text{OCl}_{10}]^{4-}$  standard has two distinctive peaks.

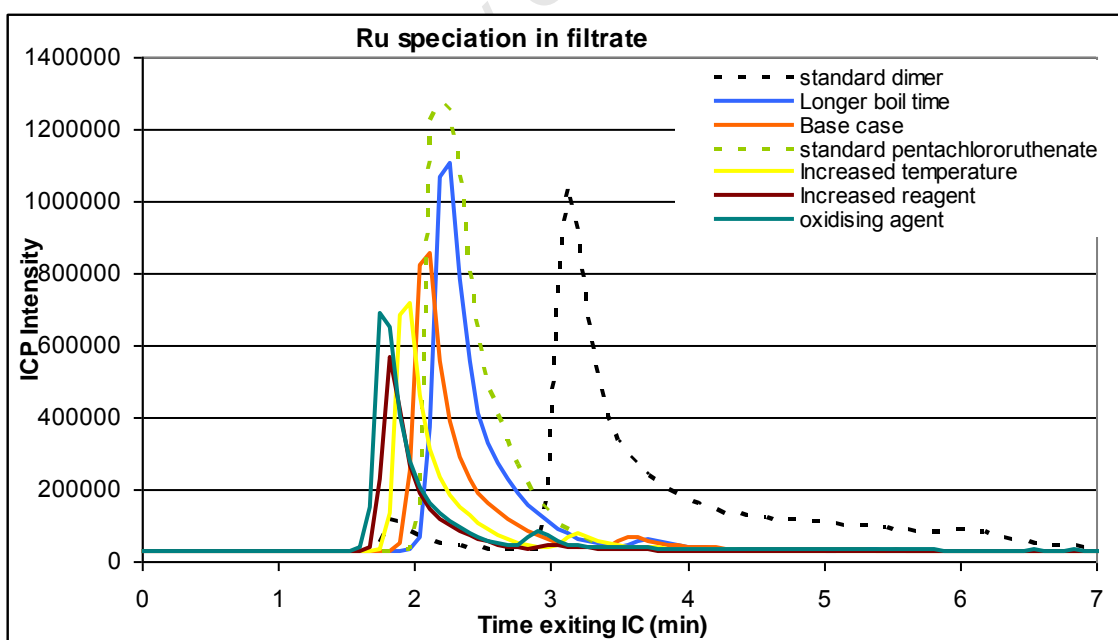
The two peaks show the existence of the monomer and dimer species. The concentration of the standard is 1 g/l and according to Table 1 the ratio of monomer to dimer will be greater than 16.2 and therefore the monomer should measure a higher intensity. The highest peak of the Ru(IV) standard is the second peak and this peak is therefore related to the monomer. This contradicts the theory about polyvalent species being retained on the column longer but it is possible for IC columns to behave differently. Therefore the first peak is attributed to the dimer and the second peak to the monomer.

The areas under the curve for the 6 M dimer standard are calculated for the initial small peak at 1.9 min and the peak at 3.1 min. By dividing the two areas, a ratio for  $[\text{RuCl}_6]^{2-} : [\text{Ru}_2\text{OCl}_{10}]^{4-}$  is calculated as 21. The literature gives a ratio of 16.2 at 2 g/l Ru. The standard is at 1 g/l and therefore a ratio of 21 is reasonable.

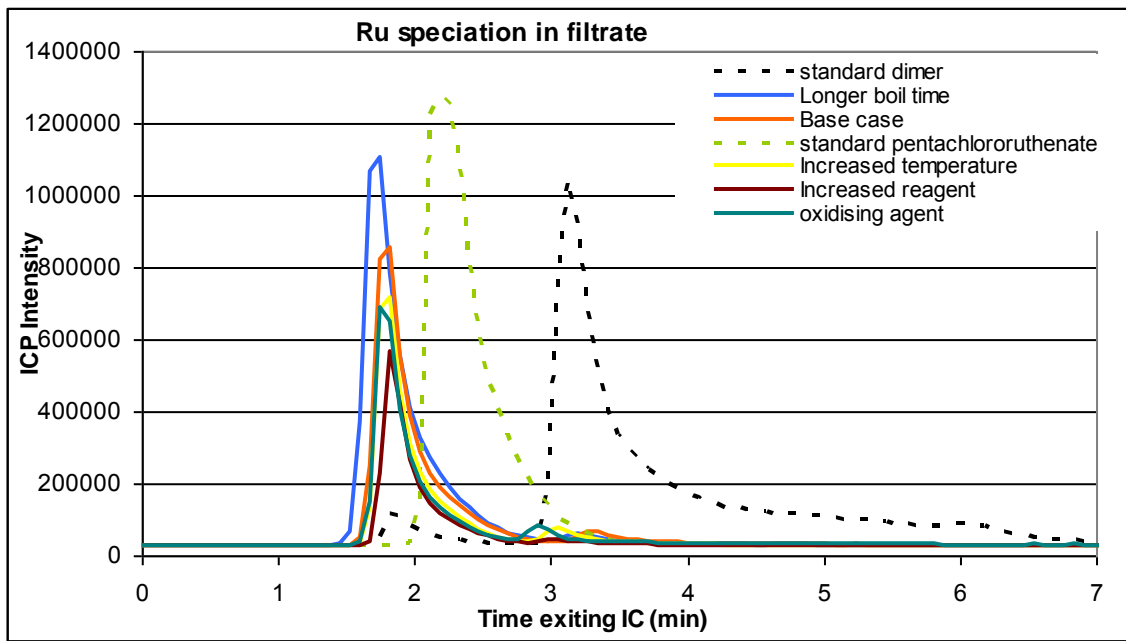
- **Effluent speciation**

The speciation profiles for the precipitation filtrate were compared to the standards in Figure 7. The profiles of the species present in the different experimental effluents indicate a drift in results, probably due to an analytical or experimental error. All the effluents have two distinctive peaks. The highest peak of the “longer boil time” experiment lies exactly on top of the pentachlororuthenate standard and the highest peaks of both the “oxidation reagent” and the “additional reagent” experiments fall exactly on the dimer standard. The second peak of the latter falls also on the second peak of the dimer standard. The second peak of the “longer boil time” experiment falls on the second peak of the pentachlororuthenate standard. It is improbable that the species in the different experiments are all different. It is more likely that a small error in the analysis occurred which shifted the species. The shift in the graphs could have been due a worn hose on the peristaltic pump used for the eluant. Another possible explanation could have been due to a pressure drop in the column. There could be several explanations for the drift in the results.

The graphs for the “longer boil time”, “base case” and the “increased temperature” experiments were slightly adjusted (by maximum 20 seconds) and the result was that all profiles fit that of the dimer perfectly. This includes the smaller peak. The result can be seen in Figure 8



**Figure 7: Speciation diagram – Effluent for the various experiment**



**Figure 8: Speciation diagram – Adjusted Ru species of the filtrate follows similar pattern to that of the standard dimer.**

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## 4 RESULTS AND DISCUSSION

The results for the different experiments are compared to the base case experiments. This ensures that the variability as a result of feed variability is eliminated. All results are tabulated in Table 5.

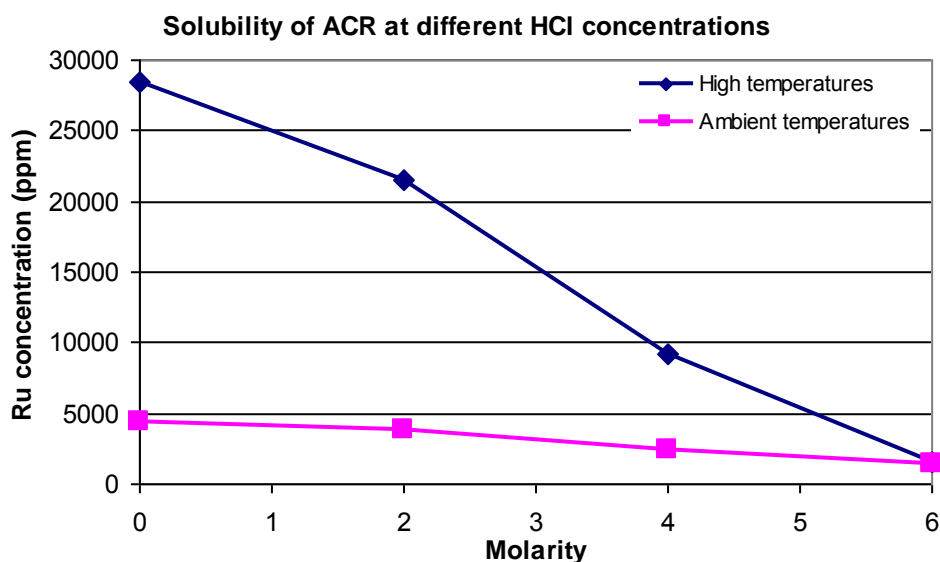
**Table 5: Yield and PSD results of all runs**

	Run 1	Run 2	Run 3	Run 4	PSD d(0.5)
Base case	98.78%	99.20%	99.29%	98.65%	81
Long boil-down	98.73%	98.43%	98.73%	98.22%	115
Higher temperature	99.17%	99.06%	99.26%	98.83%	44
Higher boil-down concentration	99.34%	99.18%	99.20%	98.73%	80
3 times excess stoichiometry	99.24%	99.10%	99.38%	99.22%	32
Base case plus H <sub>2</sub> O <sub>2</sub>	98.72%	98.79%	98.61%	98.50%	-
H <sub>2</sub> O <sub>2</sub>	98.42%	98.60%	99.08%	98.55%	35

### 4.1 ACR SOLUBILITY

ACR is highly soluble in water at ambient temperature. The solubility of ACR decreases as the molarity increases (Figure 9). At high temperatures (80°C) the ACR is highly soluble in water. The dependency of the ACR solubility on the temperature decreases as the molarity increases and at 6 M the difference is negligible.

The measured HCl molarity, after the addition of NH<sub>4</sub>Cl, for the base case experiments was 3.5 M. At this normality the measured solubility is ~ 2 300 ppm. This solubility is at ambient temperature and without any NH<sub>4</sub>Cl present. This solubility of 2 300 ppm is not a true reflection of the aqueous solution used during the ACR precipitation as the ACR solution contains many free chlorides and excess NH<sub>4</sub>Cl that hinders the ACR to dissolve.

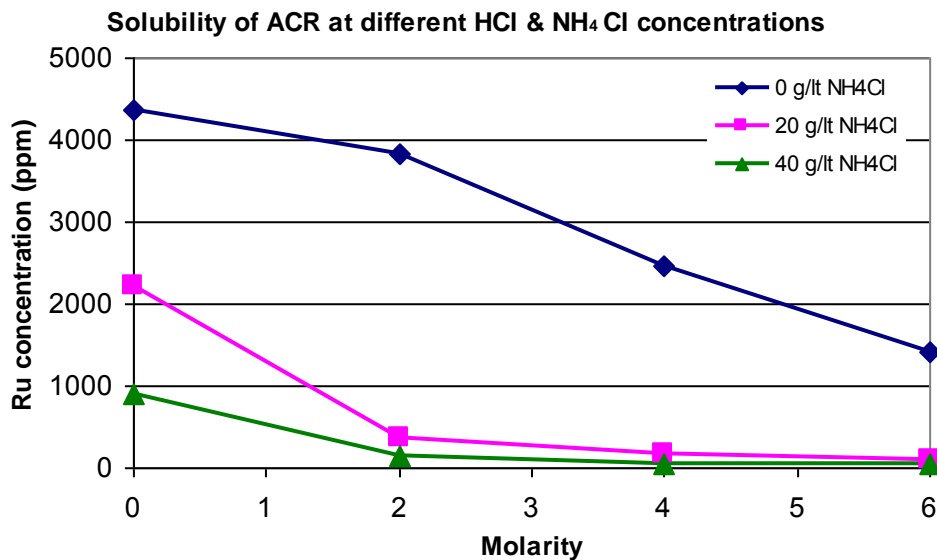


**Figure 9: Solubility of ACR at different HCl concentrations and different temperatures**

The solubility of the ACR at different  $\text{NH}_4\text{Cl}$  concentrations was also measured. The results indicate a strong dependency on the amount of  $\text{NH}_4\text{Cl}$  added. The more  $\text{NH}_4\text{Cl}$  present in the solute the less soluble the ACR due to the common ion effect. Figure 10 shows that the ACR solubility becomes less dependant on the  $\text{NH}_4\text{Cl}$  as the concentration of the HCl increases. Solubility of less than 50 ppm was achieved from 2 M to 6 M when 40 g/l  $\text{NH}_4\text{Cl}$  was added to the solute. The excess  $\text{NH}_4\text{Cl}$  present after the Ru has precipitated is at a theoretically calculated concentration of 60 g/l. Therefore the solubility of the ACR should be less than 50 ppm.

The results indicate a Ru concentration of 350 ppm and therefore there must be another factor that hinders the dissolution of the ACR. One possible factor could be that the precipitation kinetics might be slow hindering complete precipitation. Preliminary test work did not show signs of an increased yield if longer reaction times were allowed but a more formulated test should be set up testing this hypothesis.

Another possibility to lower the concentration of Ru in the filtrate is to ensure that the molarity stays at 6 M. Based on the solubility of the ACR in 6 M acid the ACR in the filtrate should be less than 50 ppm.



**Figure 10: Solubility of ACR at different HCl and NH<sub>4</sub>Cl concentrations**

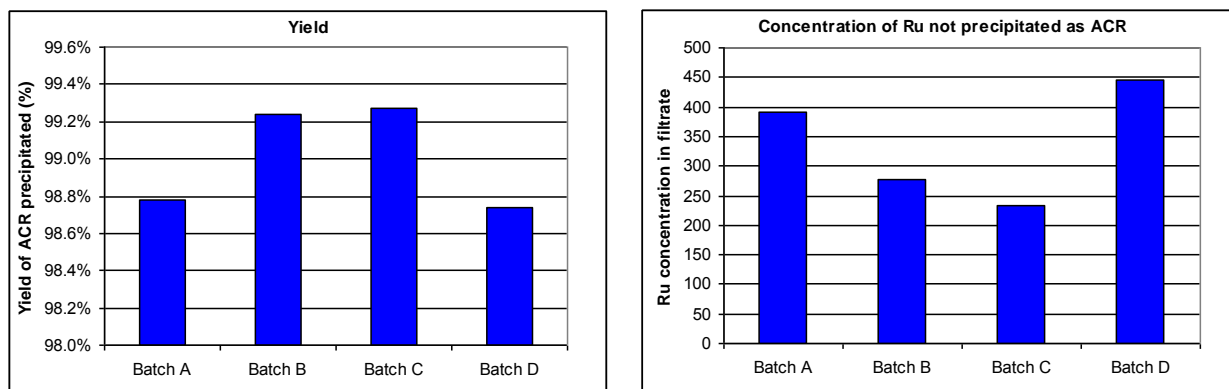
## 4.2 BASE CASE

It is noticeable (Figure 11) that the base case experiments have some variability in terms of yield and effluent concentration (standard deviation of yield = 0.4 percentage points).

This variability can be the result of a number of things:

- There are various parameters that influence the extent of precipitation reactions as described in the preceding section. Slight variation on each of these parameters can influence the yield to a small degree and give rise to the variability noted. The same amount of variability is also noticed in the PMR plant data as revealed in Figure 2.
- The variability can also result from analytical error when the samples are prepared for analysis or due to instrumental error.
- It can be due to variability in the feed that could form different species that have a higher solubility or do not react with NH<sub>4</sub>Cl. Aquation of the  $[\text{RuCl}_6]^{2-}$  and  $[\text{Ru}_2\text{OCl}_{10}]^{4-}$  species takes place at normalities below 6 M, and therefore various aquated Ru species can be present in the feed. The molarity after evaporation is 6 M and it is therefore anticipated that all aquated species would have returned to the  $[\text{RuCl}_6]^{2-}$  or  $[\text{Ru}_2\text{OCl}_{10}]^{4-}$  species. The possibility does exist that the aquated

species do not have enough reaction time to convert to the monomer or dimer species before precipitation starts.

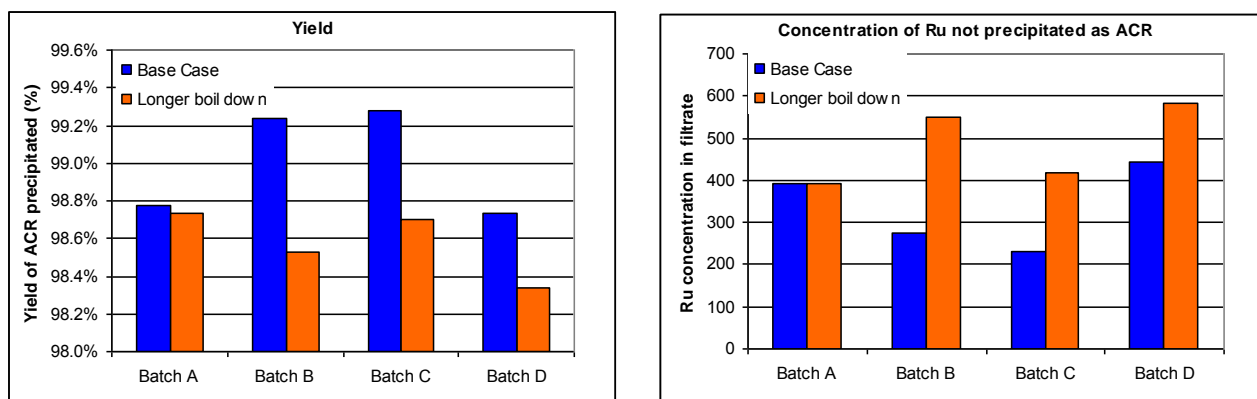


**Figure 11: Yield and Ru filtrate concentrations for base case runs**

### 4.3 LONGER BOIL-DOWN

The Ru concentration of the filtrate compared to the base case experiments is shown in Figure 12. The graphic results show a trend where the yield is lower in all 4 experiments for the runs of the long boil-down, compared to that of the base case. Statistically, the t-test confirms the observed results with a P-value of 0.03 and rejects the null hypothesis, showing that the two values are different at the 95 % confidence level. The longer boiling of the liquor gives a lower yield of 0.45 % on average.

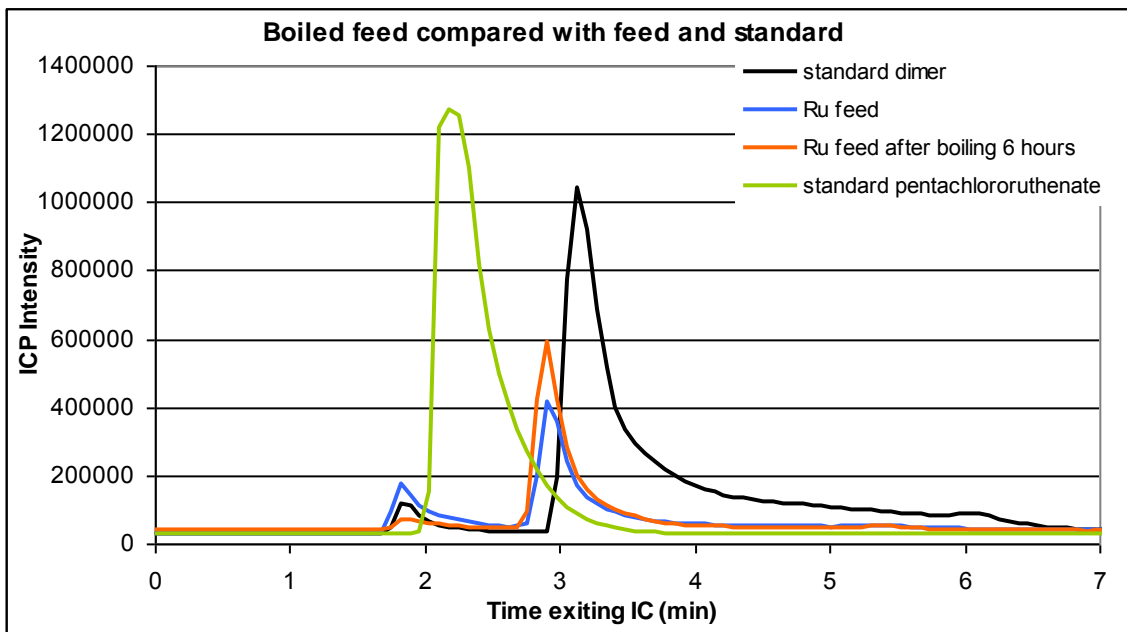
These results confirm the statistical results obtained by Engelbrecht & Phage (2008). It also suggests that the reason for the increase in yield upon the elimination of the 'Os removal' stage was the additional time at reflux temperatures. The starting concentrations and all other parameters were kept constant and only the boiling time increased. Therefore, the decrease in yield cannot be attributed to less supersaturation or any other common parameter that influences precipitation reactions. The only other explanation can therefore be linked to speciation as suggested by the hypothesis.



**Figure 12: Yield and Ru filtrate concentrations for longer boil-down experiments**

Speciation experiments were done in order to see if other species formed during the boil-down. A sample was taken from the original feed and a sample was taken after 6 hours of boiling. The speciation results are compared to the  $[\text{Ru}_2\text{OCl}_{10}]^{4-}$  and  $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$  standard in Figure 13. Noticeable from this graph is the boiled feed shows a bigger ratio of monomer to dimer in the boiled liquor compared to the feed liquor. One would expect the opposite considering that at higher Ru concentrations the dimer will be in excess (Table 1). However, before the samples were analysed through the IC, the samples are diluted to 1 g/l due to the constraints of the column. At this concentration the monomer should be in excess.

From this figure it is clear that both the feed and boiled feed resembles that of the standard. There is no evidence that shows other species, especially  $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ , forming. This is to be expected, taking into consideration that the yield is above 98 %. Even if the whole 2 % left is assumed to be a specie other than the dimer or monomer, it will difficult to notice this as a separate peak in the feed sample with the overshadowing dimer and monomer species.



**Figure 13: Speciation results indicating that the Ru feed consists of the same species as the dimer**

A similar comparison was done on the speciation of the Ru in the filtrate (shown in Figure 14). This was done to check if other species are detected in the filtrate to test the hypothesis. Therefore if any other species are detected it could be argued that a specific specie does not precipitate. The results showed that the filtrate from the longer boil-down experiment also exhibited similar speciation than that of the base case. Furthermore, both these experiments showed similar speciation to the dimer standard. The difference is that the dimer:monomer ratio was different than that of the feed. It was argued in the preceding section (section 3.5.2) that the first peak of the dimer standard represents the dimer and the second peak the monomer. In the filtrate there was more of the dimer specie present than the monomer.

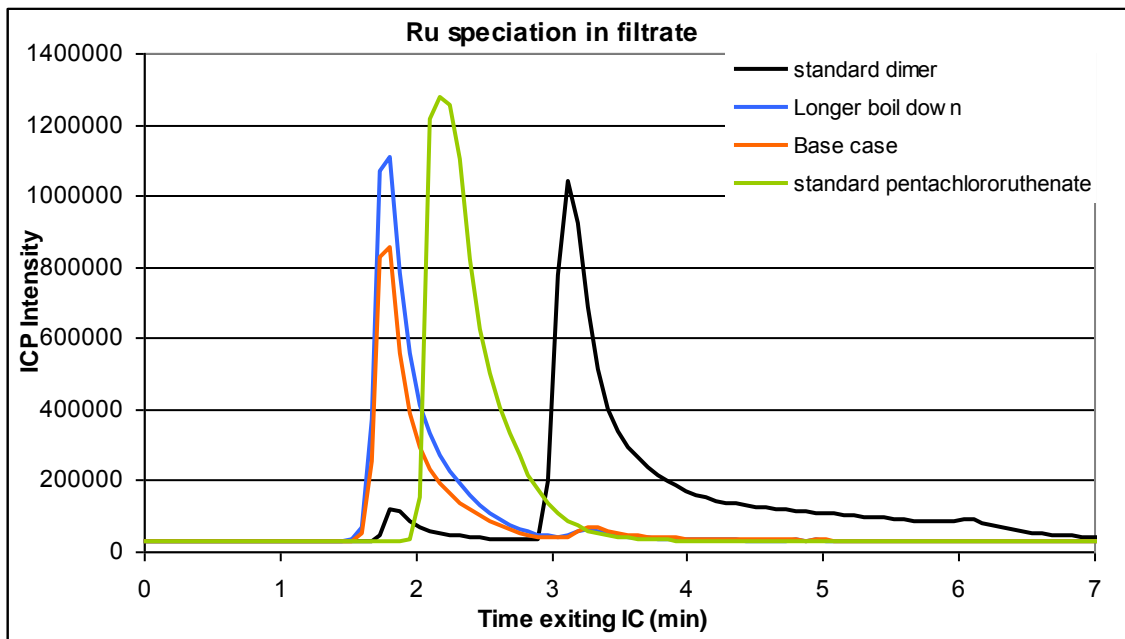
This indicates that it is the dimer specie that precipitates less than the monomer. If the assumption is made that no dimer precipitates with  $\text{NH}_4\text{Cl}$ , the yield will be much lower than 98 %. The two peaks exhibited by the feed sample in Figure 13 gives a ratio of 21 monomer to dimer. This means that 95 % of the sample is monomer. If the other 5% of the dimer is present in the feed and does not precipitate, then an efficiency of 95 % should be expected. It can therefore be concluded that the dimer does precipitate or is converted to the monomer according to the reverse reaction of equation 3 and then precipitated as  $[\text{NH}_4]_2\text{RuCl}_6$ . The opposite is also possible, where the monomer is converted to the dimer and that only the dimer precipitates.

The most likely scenario is that both the monomer and dimer precipitate, but that the dimer has a slightly higher solubility than that of the monomer. This is confirmed when looking at the crystal colour. According to Table 2 the monomer will result in a black crystal and the dimer in a dark brown crystal. The crystals formed during these tests were in majority black but a brown tint was noticed.

The literature (Table 2) suggests that the dimer is only soluble in water but the solubility was not tested in acid. However when the standard was made up in 6 M HCl, the dimer did dissolve. It then follows that the solubility of the dimer exceeds that of the monomer, which is also noticeable in Figure 14. Therefore more of the monomer is precipitated than the dimer and the specie that appears to limit the yield is the dimer.

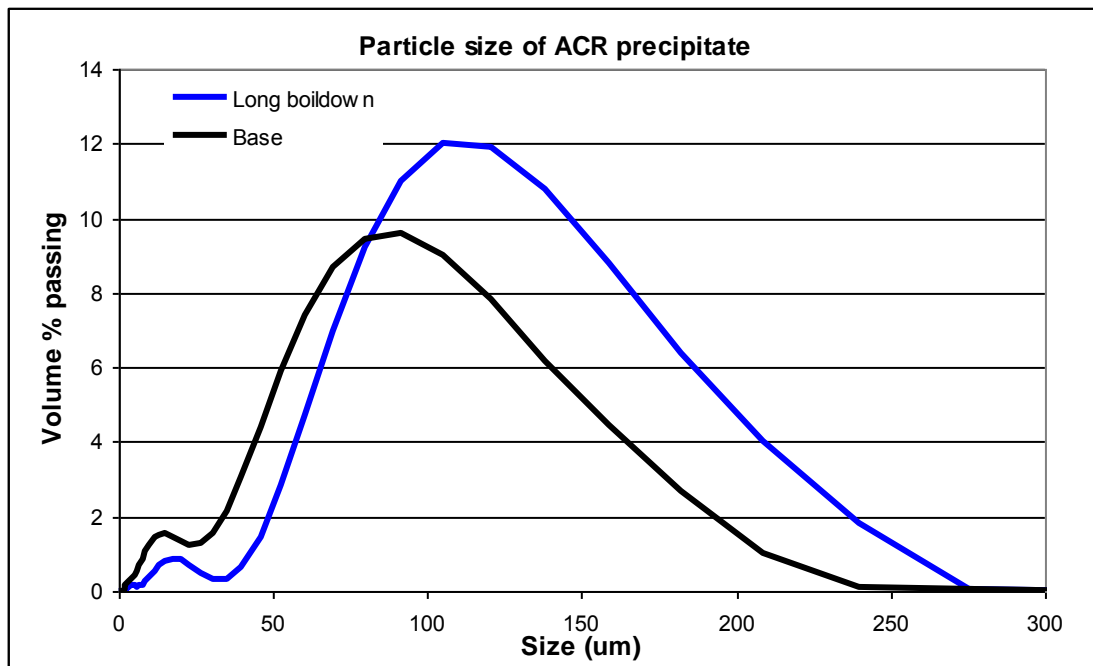
Hence the equilibrium of the monomer and dimer plays a significant role in the yield of precipitation. During the initial stages of precipitation the dimer is in excess and precipitates as the dimer. As the Ru concentration decreases the monomer forms and precipitates. However there is still an equilibrium that exist at low Ru concentrations between the monomer and the dimer. This equilibrium is reached at the endpoint of the reaction and there is no driving force left to convert the dimer to the monomer. Because of the dimer having a higher solubility than that of the monomer, mostly dimer is left in solution and this is indicated by the speciation diagrams.

Hence it is reasonable to conclude that more dimer is left in the filtrate when the experiment is boiled for longer periods. Furthermore it is possible that the reaction converting the dimer from the monomer at higher Ru concentrations has slow kinetics to reach equilibrium. Over the extended boiling period more monomer is converted to dimer which does not convert back to the monomer at the end of precipitation.



**Figure 14: Speciation results indicating that the Ru in the effluent for both the longer boil-down and the base case exhibits similar speciation than that of the dimer**

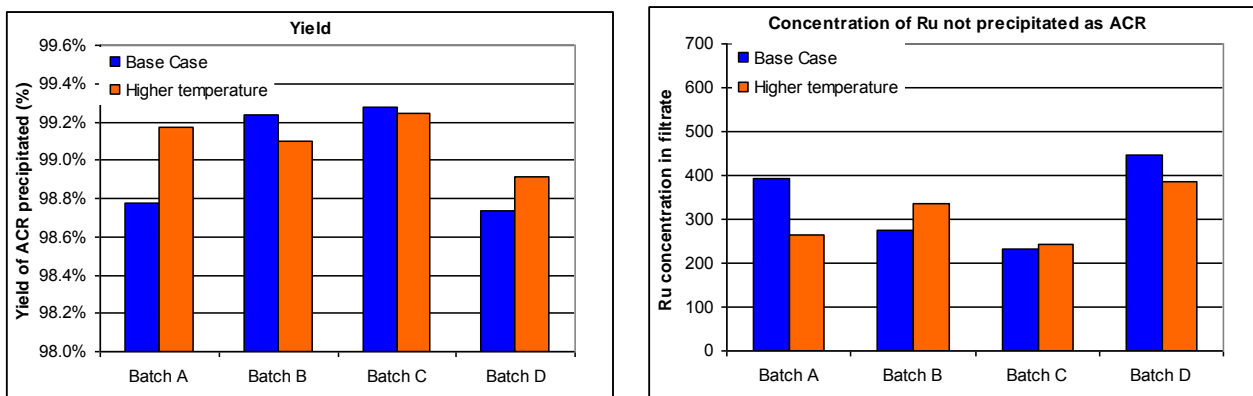
The PSD curves shown in Figure 15 of both the base case ( $d(50) = 81 \mu\text{m}$ ) and of the long boil-down ( $d(50) = 115 \mu\text{m}$ ) indicate relatively similar size distributions with two peaks. Slightly larger particles are created when the liquor is boiled for the longer period. The particle size confirms the hypothesis above that there is more dimer present as a result of the longer time at high temperatures. Because the dimer is more soluble, less supersaturation is expected when the dimer precipitates and hence larger particles form.



**Figure 15: PSD results showing larger particles for the longer boiled liquor compared to base case**

#### 4.4 HIGHER TEMPERATURE

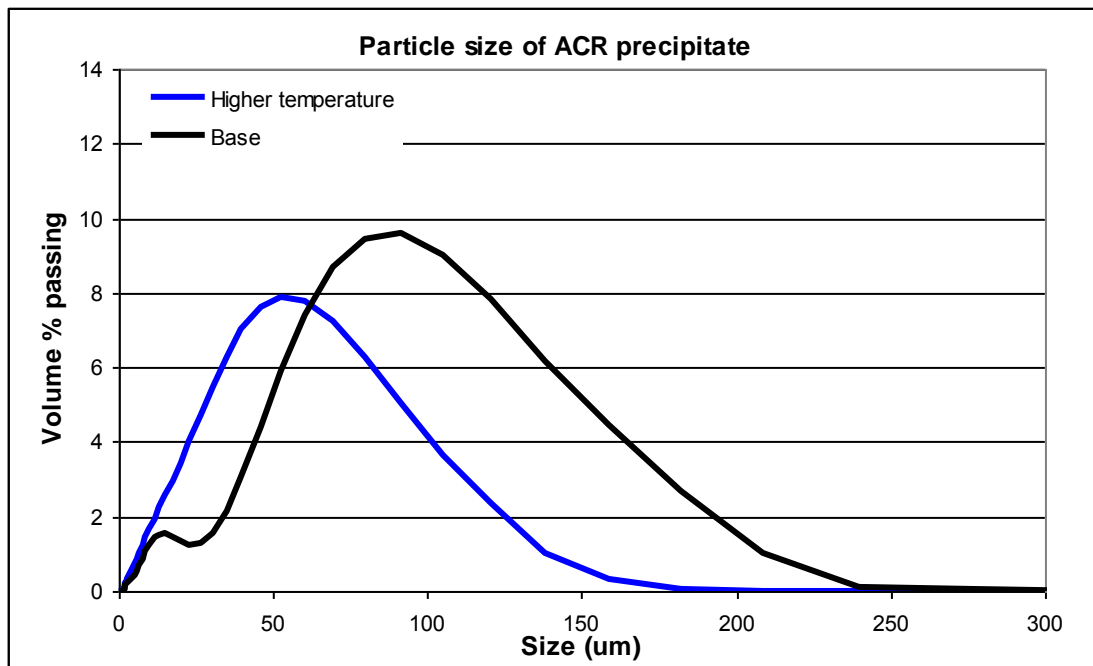
Figure 16 shows no distinct difference in the effluent concentration between the experiments carried out at 80°C and 95°C. This is confirmed with a t-test value of  $p = 0.22$  which is far greater than 0.05, therefore rejecting the null hypothesis that they are the same. These results indicate that an increase in 15°C is insignificant and does not influence the reaction. If the reaction was kinetically limited it would have proceeded further at higher temperatures because the reaction would have proceeded much faster. However, given the results, it is apparent that the reaction is already occurring at a fast pace and the 15°C increase in temperature had no significant effect. This is confirmed by Figure 9 where it is apparent that at 6 M HCl concentrations the solubility is the same at ambient and 80°C. It is therefore not expected that more ACR will be precipitated as a result of solubility.



**Figure 16: Yield and Ru filtrate concentrations for higher temperature experiments**

Figure 17 indicates a more uniform size distribution for 95°C but smaller particles overall. The PSD gives a  $d(0.5)$  of 44  $\mu\text{m}$  which is almost half that of the base case ( $d(0.5) = 81 \mu\text{m}$ ). This is contradictory to the literature where it was indicated that higher temperatures would give larger particles (Hagemann, 2003). The higher temperature could have increased the rate of nucleation, resulting in more nuclei and hence in decreasing particle size. There is a small peak visible of smaller particles in the base case showing an initial fast reaction taking place resulting in fine particles. A similar rate is seen in the higher temperature profile although this rate is similar for the complete reaction.

Following the discussion from the previous section, the higher temperature should promote the dimer to monomer equilibrium reaction. This could then explain the decrease in particle size as more monomer has formed which has a lower solubility and hence more nuclei form due to the ensuing higher supersaturation. Contradicting this hypothesis is the fact that there is no distinct indication that there is an increase in yield as a result of the 15°C increase in temperature. The results from doing the experiments at increased temperatures neither proves nor disproves that the kinetics of the conversion from the dimer to the monomer is slow.



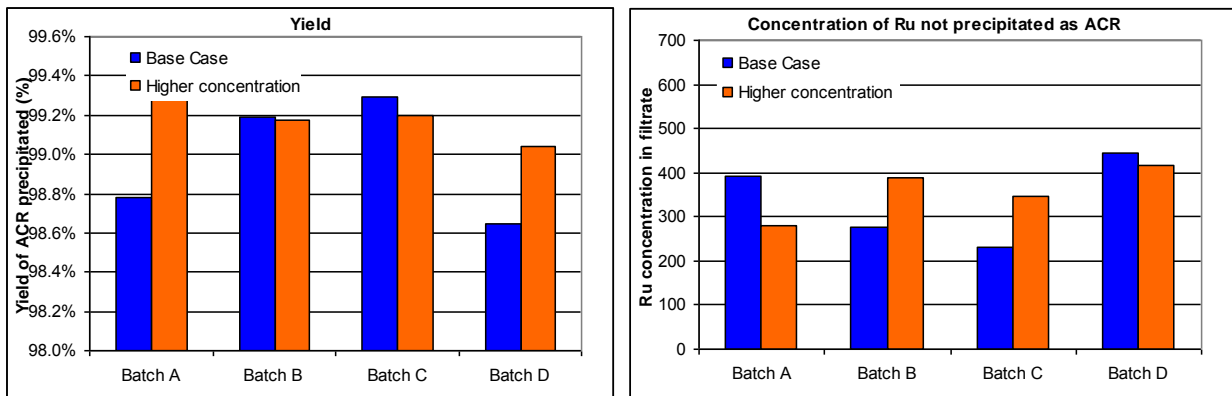
**Figure 17: PSD results showing larger particles for the higher temperature experiment compared to base case**

#### 4.5 HIGHER BOIL-DOWN CONCENTRATION

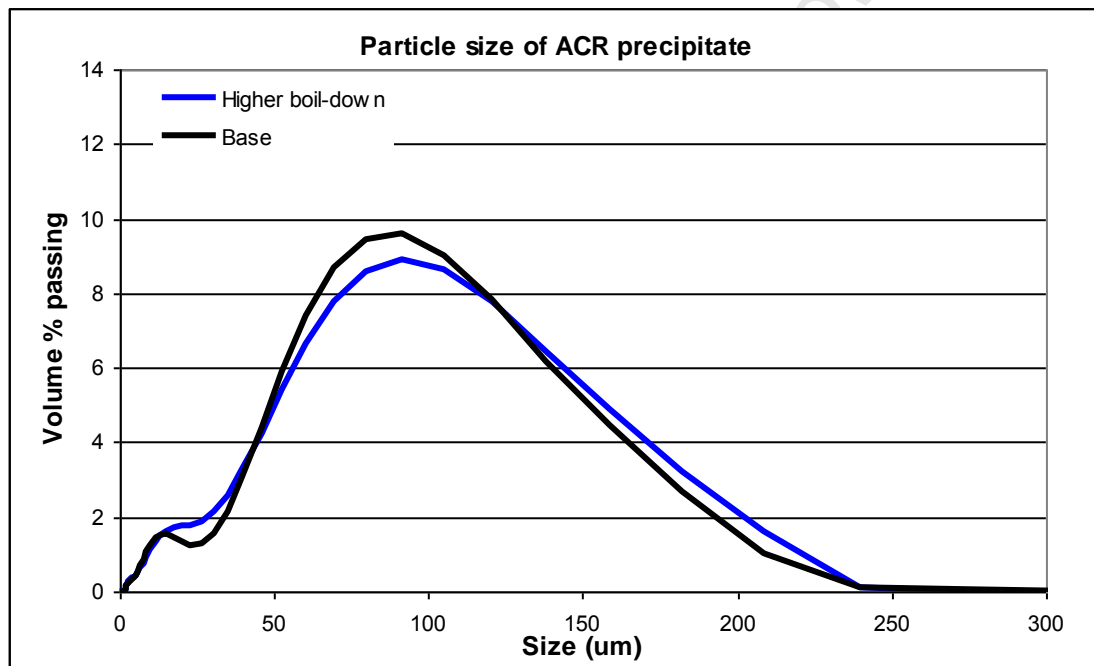
For the base case the liquor was boiled to 50 g/l and there is no dramatic difference in filtrate concentrations when compared to a boil-down concentration of 80 g/l. These results are visually displayed in Figure 18 and a t-test value of  $p = 0.14$  confirms the observed findings. The PSD also shows remarkable similarities with the particles being equally sized and distributed through the size ranges (Figure 19). The particles formed from a higher concentration has a  $d(50)$  equal to 80  $\mu\text{m}$  exactly the same as the base case with a  $d(50)$  of 81  $\mu\text{m}$ . A similar small peak is noticed on the higher boildown particle distribution diagram than that of the base case. Although not as distinct it does show an initial fast reaction producing nuclei.

It is expected from the literature that more rapid precipitation should take place if the reagents are at a higher concentration because supersaturation is increased. The higher supersaturation would then also cause finer nuclei particles to form. On the other hand, the longer time required to boil the liquor down to a higher concentration could result in more dimer formed which will result in fewer nuclei and consequently larger particles. But

because the concentration is higher it offsets this effect, leading to more or less the same size distribution and the same yield



**Figure 18: Yield and Ru filtrate concentrations for higher boil-down concentration experiments**

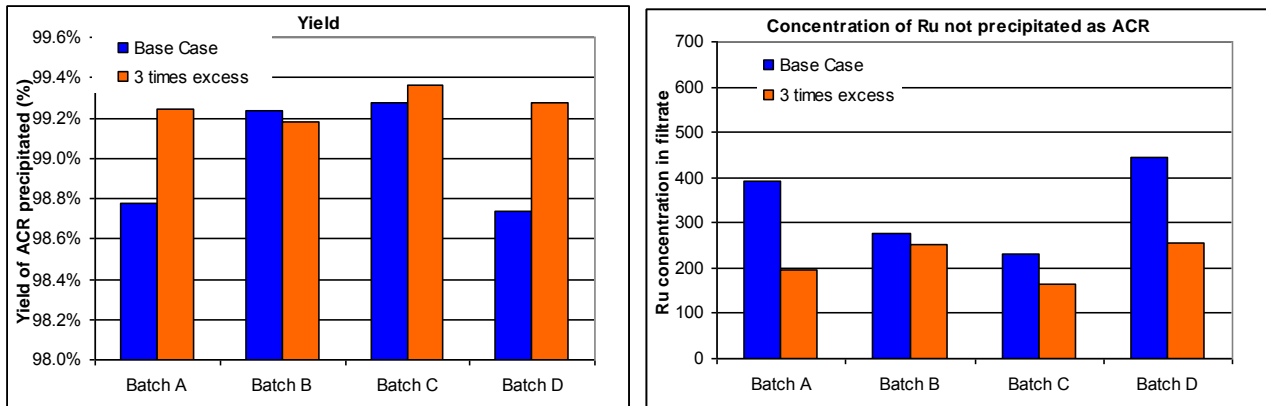


**Figure 19: PSD results showing similar particle size for the higher concentration experiment compared to base case**

#### 4.6 MORE REAGENT

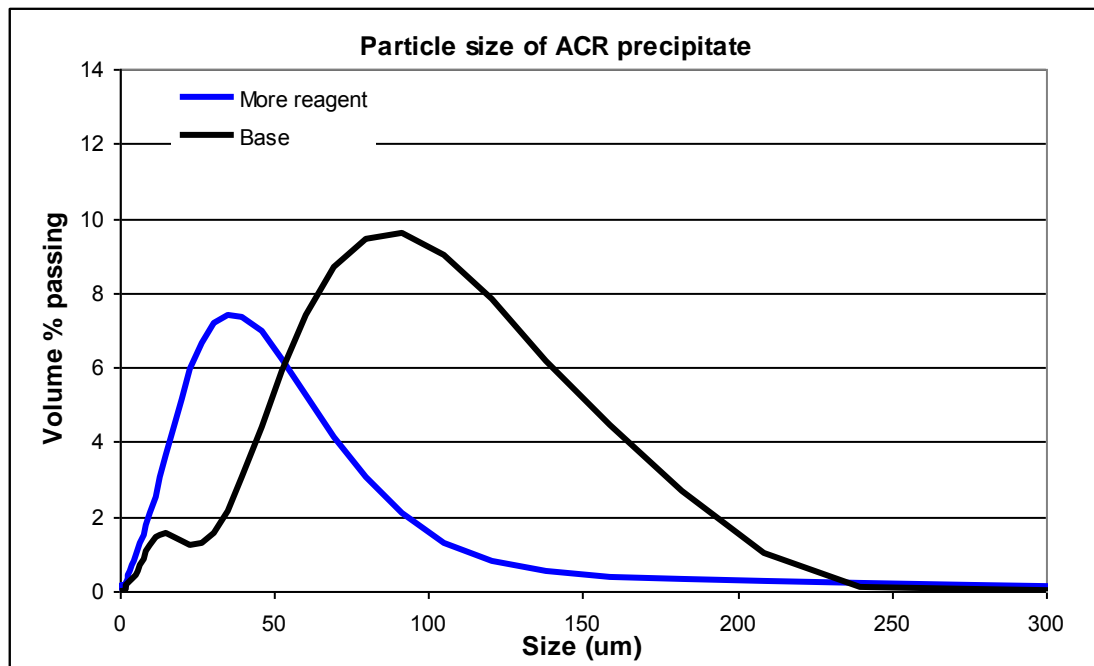
Experiments showed that the effluent Ru concentration is much lower for the experiments where more  $\text{NH}_4\text{Cl}$  was added, as represented in Figure 20. This is contrary to the yields for the base case and the additional reagent experiments. The reason is that additional reagent present in the filtrate leaves the un-precipitated Ru more diluted. Statistics confirm that the yields for the base case and the additional reagent are different within 90

% confidence (t-test value of  $P = 0.085$ ). A 95 % confidence level is required to prove that the results is different and therefore these results does not distinctively prove that there is an increase in yield. It does however show that there is an indication that there could be an increase in yield when more reagent is added.



**Figure 20: Yield and Ru filtrate concentrations for 3 times stoichiometry excess experiments**

The additional reagent resulted in a substantially decreased particle size. The PSD can be seen in Figure 21. The additional reagent produced very fine particles  $d(0.5) = 32 \mu\text{m}$  in comparison to the base case  $d(0.5) = 81 \mu\text{m}$ . The decrease in particle size shows that more nucleation takes place. This is because the addition time of the  $\text{NH}_4\text{Cl}$  was kept constant and the flow rate was increased to compensate for the additional reagent. This means that additional reagent added locally at a given time increased the supersaturation at that point, thereby giving rise to increased formation of nuclei particles.



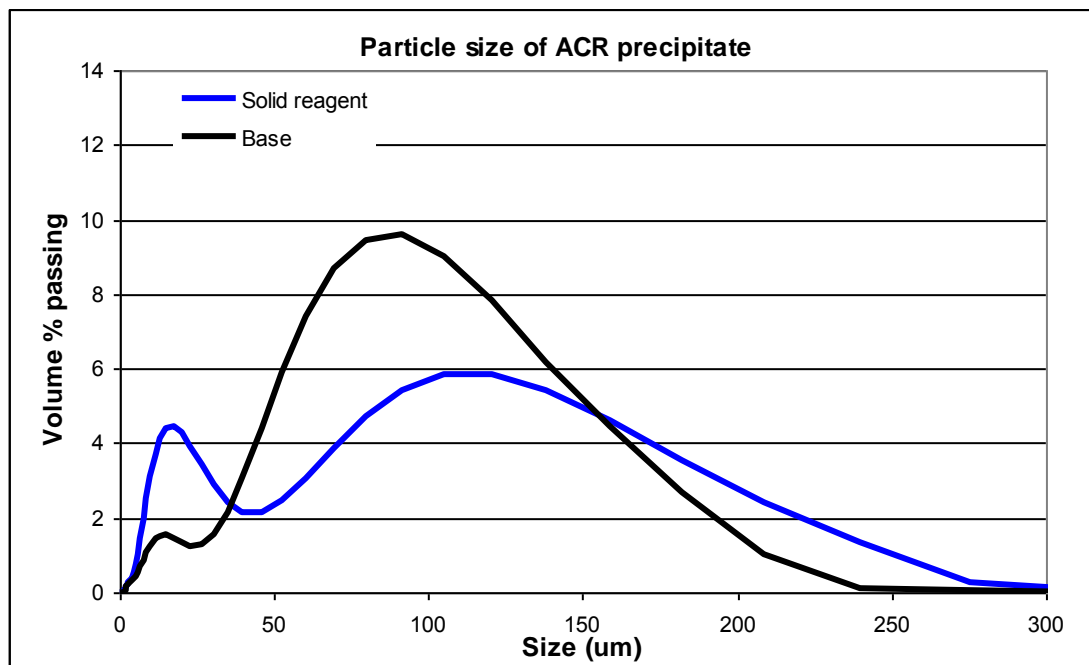
**Figure 21: PSD results showing similar particle size for the additional reagent experiment compared to base case**

The fact that the yield did not improve significantly proves that there is enough reagent available for the reaction to complete and therefore 1.5 times excess to the required stoichiometrical amount (according to equation 2) is enough reagent. This leads to the possibility that the reaction is at equilibrium even before 1.5 times the stoichiometric amount is added completely. As additional reagent is added after equilibrium is reached, it dilutes the Ru in solution further. This equilibrium should theoretically be at the solubility of ACR in the particular solution. Additional reagent could possibly dilute the solute and the ACR product can re-dissolve. This is unlikely, as was proven in section 4.1 that the solubility at high  $\text{NH}_4\text{Cl}$  concentrations is low.

The fact that the yield didn't improve even at a higher degree of local supersaturation (rate of reagent increased), but that the particle size has more than halved, means that faster addition of reagent should be avoided. It is also indicative that increasing the supersaturation by increasing the rate does not improve the yield.

A solid addition experiment was conducted where solid  $\text{NH}_4\text{Cl}$  was added to a 50 g/l boiled Ru feed liquor. The PSD (Figure 22) of the black ACR formed shows two particle size regions, similar to that of the base case. The  $d(0.5)$  is 47  $\mu\text{m}$ , which is not too small compared to the  $d(0.5) = 32 \mu\text{m}$  for the additional reagent experiment. These two regions

of particles formed could potentially indicate the presence of monomer and dimer species. The solid reagent added in one slug means that the species present will precipitate immediately. The smaller particles correspond to the monomer as the solubility is lower, while the larger particles indicate the higher solubility of the dimer.



**Figure 22: PSD results showing an initial peak with very small particles formed for the experiment of solid addition**

After the precipitate was filtered the filtrate colour was clear during the initial stages of filtration. But as the filtrate was cooled an orange/yellow crystalline residue formed on the side of the flask. This solid was filtered again and the precipitate recovered. The clear coloured filtrate was left overnight and in the morning orange-colour crystals again formed on the side of the container. It was originally suspected that these crystals are  $\text{NH}_4\text{Cl}$  that is entrained with Ru to give the coloured appearance. The yellow crystals are possibly amino ruthenate crystals that form. Usually Ru will not form complexes with  $\text{NH}_3$  due to the slow reaction kinetics. The Ru concentration in the filtrate after precipitation was 154 ppm.

These yellow crystals were dissolved in both water and acid. All crystals dissolved in water by just stirring for a couple of minutes and the liquor contained high concentrations of Ru. These crystals only slightly dissolved in 6 M HCl acid showing low concentration of Ru ion in the acidic filtrate.

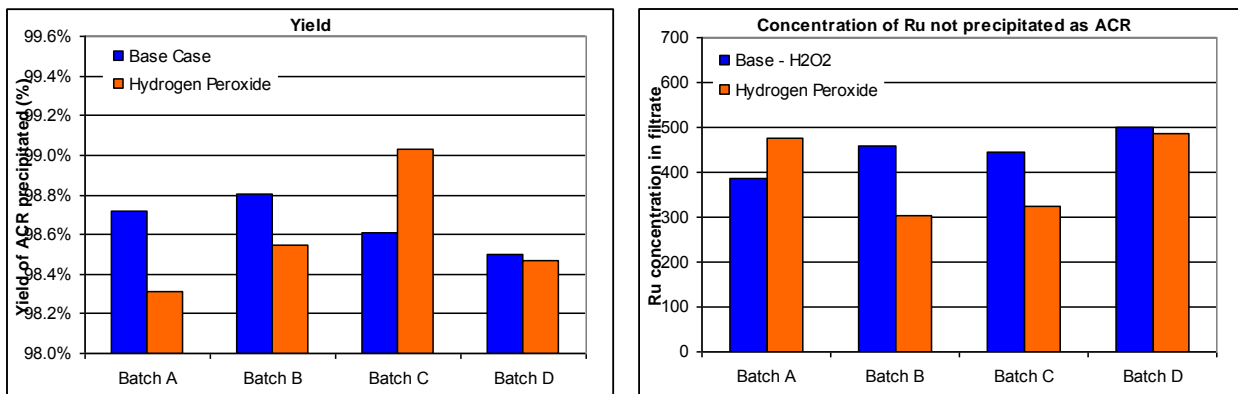
In another experiment solid  $\text{NH}_4\text{Cl}$  was added but the boiled Ru feed liquor was at a concentration of  $\pm 140$  g/l. After precipitation the Ru concentration in the filtrate was 11 ppm. No yellow crystalline product was formed. These particles were very small as filtration on Millipore was extremely slow with very high moisture content. No quantitative PSD analysis was done on the solids. The same stoichiometric amount of  $\text{NH}_4\text{Cl}$  was added and therefore this experiment indicates that it is unlikely that the  $\text{NH}_4\text{Cl}$  is a limiting reagent and that not more  $\text{NH}_4\text{Cl}$  is needed for improvement in yield. It proves that the yield is directly depended on the degree of supersaturation.

#### 4.7 OXIDISING AGENT

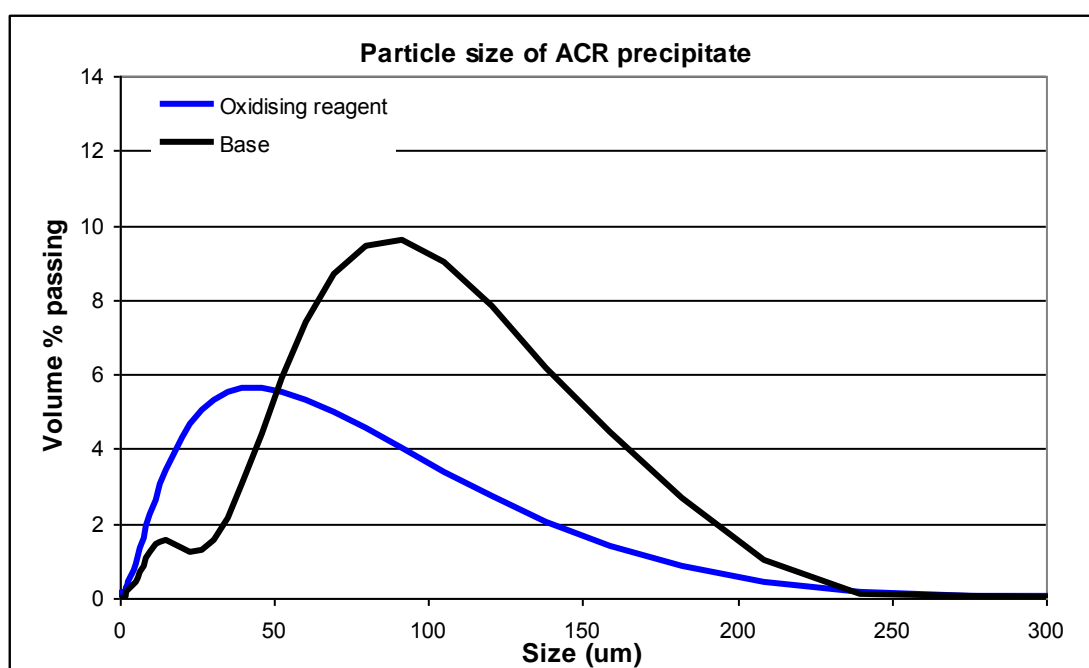
The addition of an oxidant does not show a distinct difference in filtrate concentration compared to the base case. The results can be seen in Figure 23 and the t-test yields  $p=0.36$  and therefore rejects the null hypothesis. However, the peroxide seems to have a dramatic effect on the particles size – as can be seen in Figure 24. The PSD is much more uniform for the peroxide but much smaller at the same time. The  $d(50)$  equals  $35\ \mu\text{m}$  which is much smaller than the base case, where  $d(50) = 81\ \mu\text{m}$ . This is highly peculiar as there is no reason to suspect that an increase in supersaturation would have been brought on by the addition of an oxidising agent. There could be other dynamics that affects the particle size when  $\text{H}_2\text{O}_2$  is added, for example  $\text{H}_2\text{O}_2$  could assist with breaking up the particles.

Speciation was done on a feed sample after the hydrogen peroxide was added and the Ru concentration increased. The results look very similar to that of the boiled feed after 6 hours and no distinct change or other species were noticed. These results can be seen in Figure 25 and it can be concluded that the  $\text{H}_2\text{O}_2$  has no effect on the yield or speciation of the ACR precipitation reaction.

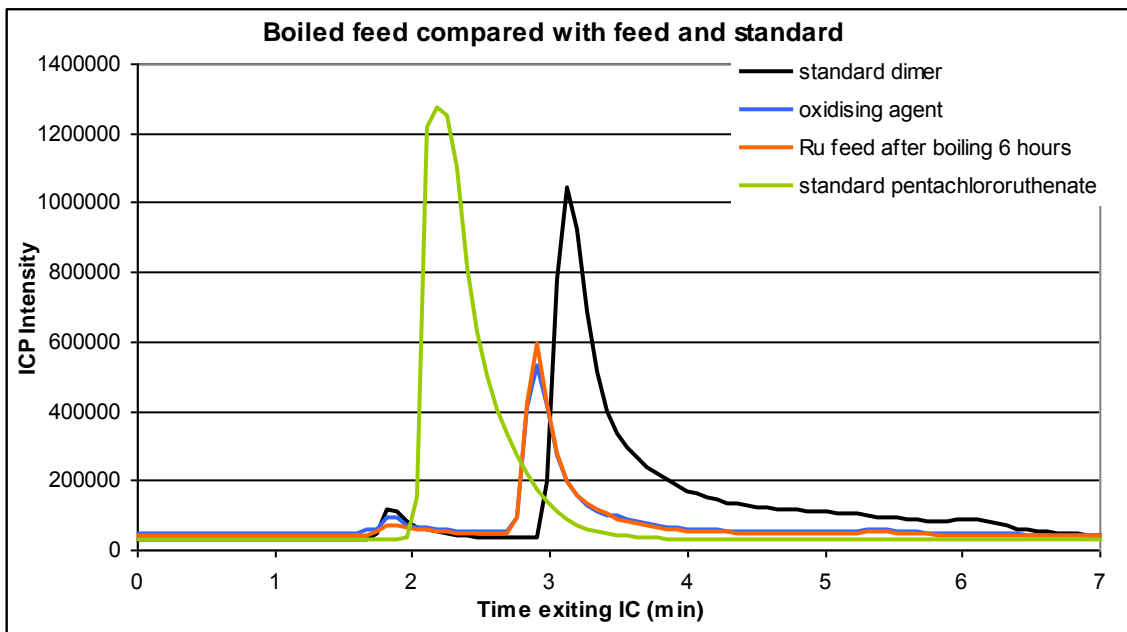
Because the peroxide does not have an effect on the yield, a possible explanation for the higher yield after discontinuing the peroxide stage in the PMR is because of the reduced time at reflux conditions.



**Figure 23: Yield and Ru filtrate concentrations for the addition hydrogen peroxide experiments**



**Figure 24: PSD results showing smaller particles for the experiment of hydrogen peroxide addition compared to base case**



**Figure 25: Speciation results indicating that the addition of peroxide had no effect on the speciation of the Ru feed after boiling for two hours**

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## 5 CONCLUSIONS

The test work was successful in identifying and proving only one of the initial hypotheses. Other beneficial conclusions were drawn which aid in understanding the ACR precipitation reaction. The following main conclusions can be drawn from the results obtained during these experiments:

- Many aquated Ru species are formed if an eluant of low HCl concentration is used when analysing species. The Ru species are much more distinct and uniform when the HCl concentration of the eluant is higher.
- The speciation diagrams of the Ru feed and of the filtrate after precipitation resemble that of the dimer standard speciation diagram. Two distinct peaks were noticed. From the literature it is expected that at low Ru concentrations the monomer specie would be in abundance and vice versa. The concentration of the dimer standard and Ru feed samples were 1 g/l and therefore the higher peak is that of the monomer. The filtrate speciation diagram show higher intensity at the dimer specie peak indicating the dimer specie limiting the extent of yield.

The filtrate after the precipitation of ACR contains the dimer specie,  $[\text{Ru}_2\text{OCl}_{10}]^{4-}$ , in abundance and only minor quantities of the monomer,  $[\text{RuCl}_6]^{2-}$ . No pentachlororuthenate,  $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ , was detected in the filtrate.

The dimer specie is more soluble than the monomer specie and hence the specie that limits more Ru to precipitate, is that of the dimer.

The monomer and dimer equilibrium in accordance to equation 3 has a significant impact on the extent of the ACR precipitation yield. Initially when the Ru concentration is high, mostly the dimer precipitates, and as the Ru concentration decreases the monomer precipitates. The equilibrium at the end of the reaction is reached when more dimer is in solution than monomer because the dimer is more soluble.

- ACR is very soluble in water but is less soluble in acid. At 6 M HCl the solubility of ACR is less dependent on temperature. The ACR solubility also decreases in solution with  $\text{NH}_4\text{Cl}$  present.

- The hypothesis that longer boil down times decreases the yield has been proven with 95 % confidence. An average yield decrease of 0.45 % has been seen when the liquor were boiled for 6 hours instead of 1.5 hours. The results indicate that more dimer is formed during the longer time spend at higher temperatures. The kinetics of the equilibrium between monomer and dimer becomes faster at higher temperatures. Longer time spend at increased temperatures promote the formation of the dimer and this leads to a decrease in yield.
- Increasing the temperature from 80°C – 95°C has a negligible effect on the yield but decreases the particle size. The PSD shows that higher temperatures increase the supersaturation but similar amounts of the dimer specie precipitates and therefore no increase in yield is noticed.
- Increasing the starting concentration from 50 g/l to 80 g/l had no significant effect on the yield of ACR precipitation or on the particle size of the ACR concluding that the change is too small to make a significant impact on yield or PSD.
- Excess reagent of 1.5 times the stoichiometric requirement is enough reagent for the completion of the reaction. Addition of more reagent has a noticeable impact on the yield however not above 95 % confidence. Smaller particles were formed during these set of experiments and is explained by the faster reagent addition rate. Increasing the rate of NH<sub>4</sub>Cl addition by 80 % decreases the particle size but do not improve the yield.
- Addition of hydrogen peroxide as oxidising agent had no effect on yield. It can be concluded that no pentachlororuthenate forms during the ACR precipitation reaction.
- Addition of a solid reagent at 140 g/l Ru gave a yield of more than 99.8 %.

The findings from these experiments gave a better understanding of the limitations of the ACR precipitation reaction. ACR is highly soluble in water and the solubility decreases with increasing HCl concentration. The solubility decreases even more in the presence of NH<sub>4</sub>Cl. Both the monomer and dimer specie precipitates with NH<sub>4</sub>Cl. The dimer specie has a higher solubility and limits the total precipitation of the ACR. Excessive time spend at high temperatures prior to precipitating ACR promotes the monomer formation and

subsequently decreases the yield. No other species are noticeable and addition of  $\text{H}_2\text{O}_2$  as oxidising agent does not increase the yield.

It is recommended that further parameters should be investigated to understand and control the equilibrium of the monomer to dimer reaction. An additional hypothesis derived from the findings is that most Ru precipitates as ACR but then re-dissolves to the solubility limit. Test work should be done on increasing the initial boil down concentration beyond 80 g/l.

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## 6 REFERENCES

- Allardyce, C.S. and Dyson, P.J. (2001) *Ruthenium in Medicine – Current uses and future prospects*, Department of Chemistry, The University of York, Heslington, United Kingdom
- Amersham Biosciences *Ion exchange chromatography - principles and methods*, ISBN 91 970490-3-4
- Anglo Platinum annual business report, (2006)
- Bassett, J.G.H. et.al. (1989) *Vogel's – Textbook of Quantitative chemical analysis*, 5<sup>th</sup> edition, Longman Scientific and technical, New York, ISBN 0-582-44693-7
- Bernardis, F.L., Grant R.A., Sherrington, D.S., (2005) *A review of methods of separation of the platinum-group metals through their chloro-complexes*, Johnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading RG4 9NH, UK, Elsevier
- Boyle, P.D. (2006) *Growing crystals that will make your crystallographer happy*, Department of chemistry, North Carolina state university
- Brits, J., Khumwenda, S. and Hagemann, J.P. (2001) *Ammonium hexachlororuthenate (ACR) precipitation and filtration optimisation*, Anglo Platinum Research Centre, SB01-251
- Cotton, F.A. and Wilkinson, G. (1972), *Advanced inorganic chemistry – a comprehensive study*, 3<sup>rd</sup> edition, Interscience publishers, United States of America.
- Dionex, (2008) IonPac AS11-HC Manual, Document No.031333-08, Dionex corporation.
- Engelbrecht, E. and Phage, K. (2008) *Ruthenium Precipitation yield in 220-Re-001*, Memorandum, Precious Metals Refinery (Pty) Ltd.
- Giulietti, M; Seckler, M.M. and Derenzo, S. (2001) *Industrial Crystallization and Precipitation from solutions: State of the Technique*, vol. 18 no.4, Brazilian Journal of Chemical Engineering
- Gösele, W. & Kind, M. (1999) *Study on the influence of mixing on the quality of continuous precipitating products*, Chemical Ing. Tech. 63.
- Grant, R (1998) *Ruthenium Chemistry PhD Studentship*

<http://platinum.preciousmetalinvestment.com/ruthenium/uses-of-ruthenium/> (15 October 2010)

Hagemann, J.P. (2003), *The production of rhodium via the DETA route*, Anglo Platinum Research Centre, Germiston, M/RD/PP/PMR/05/R 0544/R

Hagemann, J. (2007), *Ammonium Chloro Ruthenate Precipitation Yields*, Memorandum, Precious Metals Refinery (Pty) Ltd

Hagemann, J. (2008), Personal Communication, Technical Manager, PMR

Johnson Matthey “PGM prices”, <http://www.platinum.matthey.com/pgm-prices/price-charts/> [2010, December 4]

Jones. P. and Schwedt. G. *Anal. Chim. Acta* 220 (1989) 195.

Lewis, A. (2008) *Crystallization and precipitation: Understanding industrial purification processes*, Hydrometallurgy MSc coursework, University of Cape Town Chemical Engineering department

Manning, T.J. and Grow, W.R. (1997), *Inductively Coupled Plasma – Atomic Emission Spectrometry*, Department of Chemistry, Valdosa State University.

Mersmann, A. (1999) *Crystallization and precipitation*, Department B of Chemical Engineering – Technical University Munich, Chemical and Processing; Elsevier

Rard, J.A. (1984) *Chemistry and thermodynamics of ruthenium and some of its inorganic compounds and aqueous species*; Lawrence Livermore National Laboratory, University of California

Perry, R.H. and Green, D.W. (1997) *Perry's chemical engineering's handbook*, 7<sup>th</sup> edition, McGraw-Hill international editions, ISBN 0-07-115982-7

Precious metal investment, “Uses of Ruthenium”, <http://platinum.preciousmetalinvestment.com/ruthenium/uses-of-ruthenium/> [2010, September 15]

Precious metals refinery (2010), *Operational work instruction – Area 220 Ruthenium side stream*, *Precious metals refinery*, Document Management system (DMS), Rustenburg, South Africa.

Pshenitsyn, N.K. and Ezerskaya, N.A. (1960) *Preparation and Polarography of Complex Ruthenium Chlorides*, Russian Journal of Inorganic Chemistry

Rechnitz, G.A. and Goodkin, S.C. (1963) *Some Properties of Ruthenium(III) and (IV) in Acid Solution – A review of recent research*, Department of Chemistry, University of Pennsylvania

Sathyamoorthy, S; Hounslow, M.J. and Moggridge G.D. (2000) *Influence of stirrer speed on the precipitation of anatase particles from titanyl sulphate solution*, Department of Chemical Engineering – University of Cambridge,

Seddon, E.A. and Seddon, K.R. (1984), *The chemistry of Ruthenium – Topics in organic and general chemistry*, Monograph 19, Elsevier, Amsterdam

Shugar, G.J. and Ballinger J.T. (1996), *Chemical Technician's ready reference handbook*, McGraw-Hill, Inc., ISBN 0-07-057186-4

Skoog D.A., Holler F.J. and Nieman T.A. (1998), *Principles of instrumental analysis*, 5<sup>th</sup> edition, Saunders College Publishing, ISBN 0-03-002078-6

Taqi Khan M.M; Ramachandraiah, G. and Shukla, R.S. (1988) *Ruthenium(III) Chloride in Aqueous Solution: Kinetics of the Aquation and Anation Reactions of the Chloro Complexes*, Inorganic Chemistry

Viljoen, K. (2003), *Ruthenium(III) Aqua Chloro complex chemistry: The interconversion of Hexachlororuthenate(III) and Aquapentachlororuthenate(III) Species*, MSc in chemistry, University of Stellenbosh, South Africa

Weiers, R.M. (2008), *Introduction to business statistics*, Thompson Southern-Western, ISBN-13: 778-0-324-38144-3

Weiss. J. 2004, *Handbook of Ion Chromatography, Third, Completely Revised and Enlarged Edition*, WILEY-VCH Verlag GmbH & Co. KGaA Weinheim, ISBN: 3-527-28701-

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## 7 APPENDIX

### 7.1 Experimental results

Table A1: Experimental Batch A

	<b>Base</b>	<b>Longer boil down</b>	<b>Higher temperature</b>	<b>Higher boil down concentration</b>	<b>3 times stoichiometric</b>
Start volume (ml)	1000	1000	1000	1000	1000
Start concentration (ppm)	26000	26000	26000	26000	26000
Start Ru mass (g)	26.0	26.0	26.0	26.0	26.0
Boil down time (min)	105	385	110	135	105
Boil down volume (ml)	520	520	520	325	520
Boil down concentration (g/l)	50	50	50	80	50
Boil down sample volume (ml)	10	10	10	10	10
Boil sample (ppm)	47300	49500	47080	77660	48730
NH <sub>4</sub> Cl added (ml)	300	300	300	300	500
NH <sub>4</sub> Cl addition time (min)	45	45	45	45	65
Temperature (°C)	80	80	95	80	80
Filtrate sample (ppm)	392	392	266	279	195
Filtrate Ru mass (g)	0.32	0.32	0.22	0.17	0.20
Yield (%)	98.78%	98.78%	99.17%	99.34%	99.24%

Table A2: Experimental Batch B

	<b>Base</b>	<b>Longer boil down</b>	<b>Higher temperature</b>	<b>Higher boil down concentration</b>	<b>3 times stoichiometric</b>
Start volume (ml)	1000	1000	1000	1000	1000
Start concentration (ppm)	30811	30811	30811	30811	30811
Start Ru mass (g)	30.8	30.8	30.8	30.8	30.8
Boil down time (min)	90	375	90	115	90
Boil down volume (ml)	620	620	620	390	620
Boil down concentration (g/l)	50	50	50	80	50
Boil down sample volume (ml)	10	10	10	10	10
Boil sample (ppm)	53823	52228	53185	84667	54868
NH <sub>4</sub> Cl added (ml)	300	300	300	300	500
NH <sub>4</sub> Cl addition time (min)	45	45	45	45	65
Temperature (°C)	80	80	95	80	80
Filtrate sample (ppm)	274	534	320	374	250.5
Filtrate Ru mass (g)	0.25	0.49	0.29	0.25	0.28
Yield (%)	99.19%	98.42%	99.05%	99.17%	99.10%

Table A3: Experimental Batch C

	<b>Base</b>	<b>Longer boil down</b>	<b>Higher temperature</b>	<b>Higher boil down concentration</b>	<b>3 times stoichiometric</b>
Start volume (ml)	1000	1000	1000	1000	1000
Start concentration (ppm)	27500	27500	27500	27500	27500
Start Ru mass (g)	27.5	27.5	27.5	27.5	27.5
Boil down time (min)	80	360	85	120	85
Boil down volume (ml)	550	550	550	345	550
Boil down concentration (g/l)	50	50	50	80	50
Boil down sample volume (ml)	10	10	10	10	10
Boil sample (ppm)	46970	49929	48444	76230	47850
NH <sub>4</sub> Cl added (ml)	300	300	300	300	500
NH <sub>4</sub> Cl addition time (min)	45	45	45	45	65
Temperature (°C)	80	80	95	80	80
Filtrate sample (ppm)	232	416	242	348	165
Filtrate Ru mass (g)	0.19	0.35	0.20	0.22	0.17
Yield (%)	99.29%	98.73%	99.26%	99.20%	99.38%

Table A4: Experimental Batch D

	<b>Base</b>	<b>Longer boil down</b>	<b>Higher temperature</b>	<b>Higher boil down concentration</b>	<b>3 times stoichiometric</b>
Start volume (ml)	1000	1000	1000	1000	1000
Start concentration (ppm)	27823	27823	27823	27823	27823
Start Ru mass (g)	27.8	27.8	27.8	27.8	27.8
Boil down time (min)	90	360	90	125	90
Boil down volume (ml)	555	555	555	350	555
Boil down concentration (g/l)	50	50	50	80	50
Boil down sample volume (ml)	10	10	10	10	10
Boil sample (ppm)	50968	5100	50073	79663	46580
NH <sub>4</sub> Cl added (ml)	300	300	300	300	500
NH <sub>4</sub> Cl addition time (min)	45	45	45	45	65
Temperature (°C)	80	80	80	80	80
Filtrate sample (ppm)	445	584	384	418	256
Filtrate Ru mass (g)	0.38	0.49	0.32	0.27	0.27
Yield (%)	98.65%	98.23%	98.83%	99.04%	99.04%

Table A5: H<sub>2</sub>O<sub>2</sub> experiments

	Base case (i)	H <sub>2</sub> O <sub>2</sub> (i)	Base case (ii)	H <sub>2</sub> O <sub>2</sub> (ii)	Base case (iii)	H <sub>2</sub> O <sub>2</sub> (iii)	Base case (iii)	H <sub>2</sub> O <sub>2</sub> (iii)
Start volume (ml)	1000	1000	1000	1000	1000	1000	1000	1000
Start concentration (ppm)	21994	21994	32241	32241	28115	28115	29344	29344
Start Ru mass (g)	22.0	22.0	32.2	32.2	28.1	28.1	29.3	29.3
Boil down time (min)	90	85	90	90	95	90	90	95
Boil down volume (ml)	440	440	645	645	560	560	590	590
Boil down concentration (g/l)	50	50	50	50	50	50	50	50
Boil down sample volume (ml)	10	10	10	10	10	10	10	10
Boil sample (ppm)	50061	46629	49500	52415	49830	48730	51194	52679
H <sub>2</sub> O <sub>2</sub> added (ml)	0	50	0	50	0	50	0	50
NH <sub>4</sub> Cl added (ml)	300	300	300	300	300	300	300	300
NH <sub>4</sub> Cl addition time (min)	45	45	45	45	45	45	45	45
Temperature (°C)	80	80	80	80	80	80	80	80
Filtrate sample (ppm)	386	475.5	412	477	459	303	501	484.5
Filtrate Ru mass (g)	0.28	0.37	0.39	0.47	0.39	0.27	0.44	0.45
Yield (%)	98.72%	98.31%	98.81%	98.54%	98.61%	99.03%	98.50%	98.46%

## 7.2 ACR solubility results

Table A6: Solubility experiments

	High temperatures	0 g/lit NH <sub>4</sub> Cl	20 g/lit NH <sub>4</sub> Cl	40 g/lit NH <sub>4</sub> Cl
NH <sub>4</sub> Cl added (g)	0	0	1	2
stirring time (hrs)	2	2	2	2
ACR added (g)	10	10	10	10
Temperature (°C)	80	25	25	25
Concentration (ppm) of Ru after dissolving				
0 M HCl	28425	4372	2223	903
2 M HCl	21529	3837	369	144
4 M HCl	9185	2467	165	51
6 M HCl	1559	1414	102	42