RECOVERY OF PGMs FROM A COPPER OXIDISING LEACH RESIDUE

RUSTENBURG BASE METAL REFINERY

ANGLO PLATINUM

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DECLARATION

I declare that this thesis, submitted for the degree of Master of Science in Applied Science at the University of Cape Town is my own work except where otherwise referenced. It has not been submitted prior to this at any other university for any other degree or examination.

ABSTRACT

The primary purpose of this work is to develop, test and evaluate a process for treating a copper oxidation pressure leach residue, likely to arise in the context of Anglo Platinum's proposed Base Metal Refinery expansion. The elements contained in this residue are predominantly the platinum group metals (PGMs), copper, nickel, zinc, tin, antimony, bismuth, manganese, silver, arsenic, tellurium, lead, selenium, silica and sulphur. A process is required that can be used to separate PGMs from base metals and sulphur, thereby giving a PGM-rich product suitable for immediate further processing in the Precious Metals Refinery.

The process proposed here involves an oxidative caustic leach to remove elemental sulphur from the residue feed material, then treatment via a copper polishing pressure leach, thereby providing a suitable degree of separation of the abovementioned elements from the platinum group metals and upgrading the platinum group metals content as much as possible. Although the focus is on the recovery of PGMs, recommendations also will be made regarding the recovery of other elements like selenium and tellurium.

The work presented describes test work investigating the effect of a variety of parameters on the leaching behaviour of the material during both the caustic and the sulphuric acid pressure leach. For the caustic leach the effect of temperature, reactor residence time, caustic strength and solid loading were investigated. For the pressure leach the effects of temperature, oxygen partial pressure, initial acid strength, initial addition of ferrous iron and agitation rate were investigated.

The oxidative caustic dissolution of elemental sulphur is rapid, while very little of the other metals are dissolved. The pressure acid leach work indicated a complex network of dissolution mechanisms relating to the interaction of elemental sulphur formation, which forms inhibitive layers around the minerals, and its oxidation to sulphate by both oxygen and ferric iron. The overall rate of leaching is determined by the effect temperature, oxygen partial pressure and ferrous iron addition have on this interaction.

It has been demonstrated during this test work that an overall mass loss of undesirable elements from the feed material above 90% is achievable. Copper, nickel, iron and sulphur extractions above 97% can be achieved, with minimal extraction of the PGMs in the material. This test work also indicates that Se, Te and Pb can be extracted at levels above 60% in the proposed two step process: A 20 minute atmospheric NaOH leach at 80°C, followed by a 4 hour, low temperature (110 °C) sulphuric acid pressure leach is proposed as the process to successfully concentrate the contained PGM portion of this material relative to the feed. Recommendations for further test work are also made regarding any other valuable metals recovery.

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On a more personal note, to my wife Sonja and my kids, Felicia and Ian, thank you for the sacrifices you have made to help make this goal achievable.

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LIST OF ABBREVIATIONS

BMR	Base metal refinery
CPL	Copper Pressure Leach
EAF	Electric arc furnace
FIC	Final concentrate
MEC	Magnetic leach concentrate
NOX	Non-oxidising leach
NCM	Nickel copper matte
PGM	Platinum group metals and gold
PMR	Precious metals refinery
PVL	Pressure vessel liquor
SLR	Secondary leach residue
STR	Selenium and tellurium removal

SECTION 1

INTRODUCTION AND PROBLEM STATEMENT

Anglo Platinum’s expansion programme to 3.5 million oz/annum of platinum has necessitated expansion of its Base Metal Refinery to accommodate the associated increase in throughput of nickel and copper. The Base Metal Refinery in its current configuration has a name plate capacity of 21 500 t/a of nickel and this is envisaged to increase to beyond 30 000 t/a. Initial cost estimates indicated that the best business case for expanding the output of the current refinery would be a brownfield retrofit and installation of an atmospheric leach and iron removal step. The current nickel tank house needs to be converted to a copper tank house, and a completely new nickel tank house needs to be installed.

The detailed flow sheet and purpose of the relevant changes to the current Base Metal Refinery are beyond the scope of this document, but general flow sheets are shown in Figures 1 and 2.

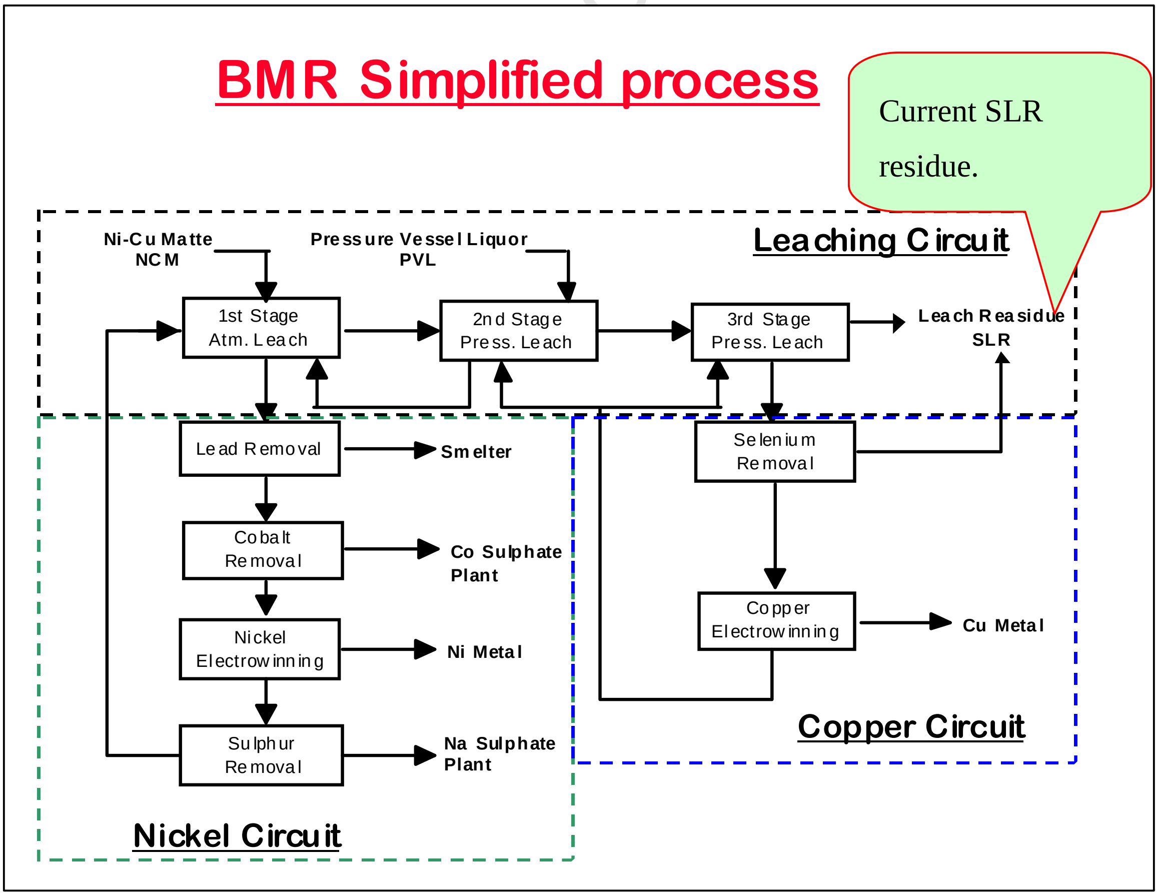


Figure 1: Current BMR Flow sheet

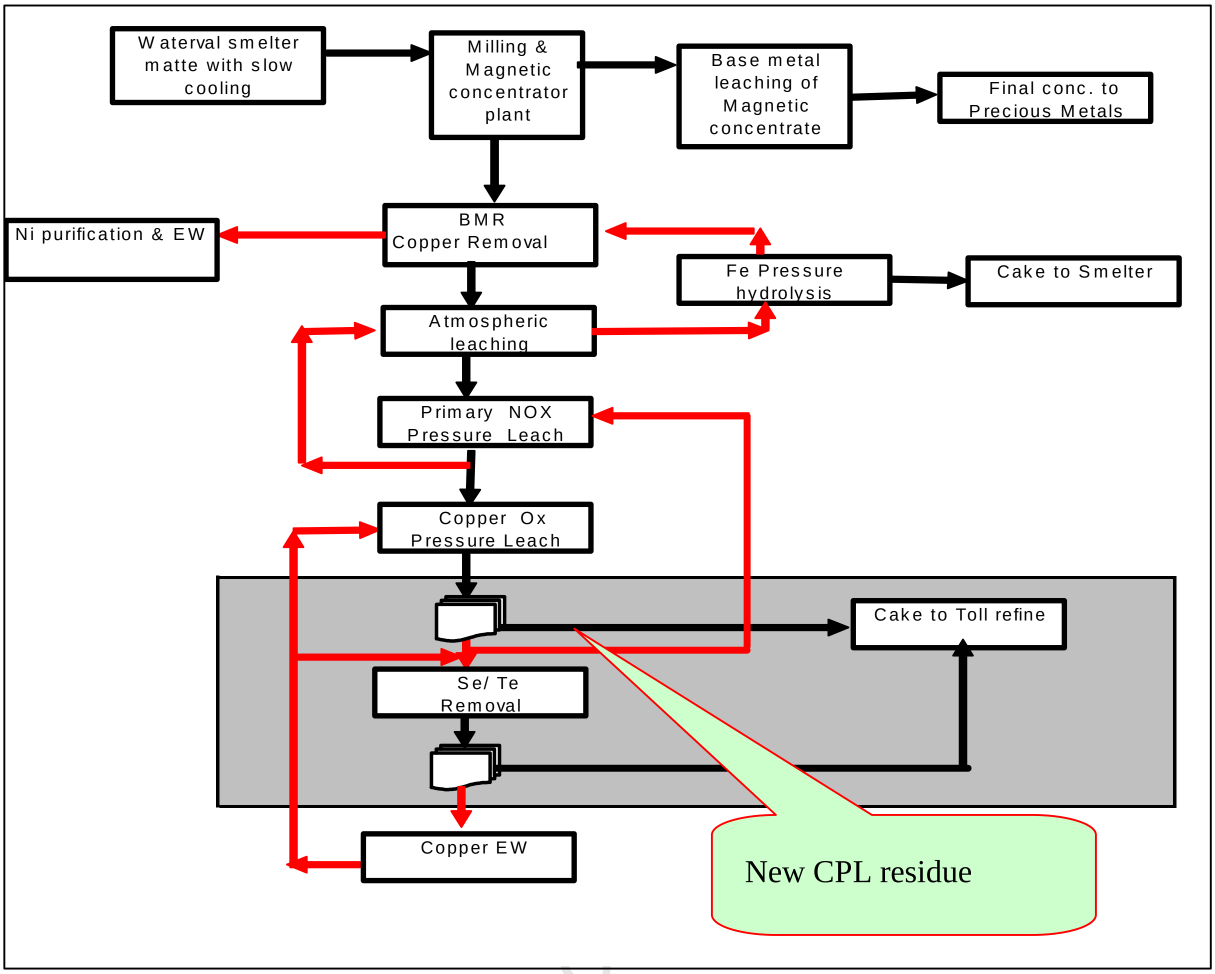


Figure 2: New BMR flowsheet

In the current process, as shown in **Figure 1**, the purpose of the secondary leach is to oxidise the copper and the remaining nickel not leached in the primary leach, and further, it is the only outlet for iron from the BMR. It is also an outlet for a whole range of elements that would be regarded as impurities in the Precious Metals Refinery and therefore need to be removed to maintain balance in the whole refineries circuit. The assay results indicated in **Table 1 (SLR)** are a combined residue from the selenium removal stage and the 3rd stage pressure leach. The major components of this residue are iron and copper. The secondary leach residue (SLR) is currently generated at a rate of approximately 550 t/m and it is sent for toll refining. The associated transport costs, toll refining costs and interest lost on trace PGMs locked up in the SLR provided an incentive to consider changes to the current residue removal circuit.

The first step in the new process **(see Figure 2)** is to separate iron out in the NOX pressure and atmospheric leach stages of the process and return the iron containing cake to the smelter. The NOX residue is then leached in order to remove as much of the nickel and copper as possible in the CPL stage. The new secondary leach or copper pressure leach (CPL) residue, as it is referred to, still contains mostly the same elements as the SLR, although very little iron, resulting in a mass reduction from 550 t/month to approximately 140 t/month residue. The new BMR process flow sheet **(Figure 2)** was evaluated under a continuous test work programme, during which there were two distinct periods. During period A no extra Fe was added to the CPL leach as co-oxidant (beside oxygen), while in period B small amounts of ferrous ions were added in order to enhance the leaching kinetics. The continuous test work programme showed that when Fe was added to the CPL leach, much better leaching kinetics of copper and nickel could be achieved. This then led to a process design where a small amount of Fe would be added to the CPL leach, and because of the better leaching kinetics, only one additional autoclave would need to be installed in order to handle the 60% increase in refinery output. The analysis of the residues produced during these two periods is given in **Table 1**.

The large mass reduction in the residue between the current process and the new BMR process and the subsequent increase in the proportion of PGMs being toll refined necessitated an investigation into possible treatment routes for this residue. Potentially, the next step in the process would be to separate the contained PGMs from this residue so that it could be treated in-house. Doing a mass distribution of elements in the various streams during continuous test work trials showed that 95–98% of the PGM input into the new process would be contained in the CPL residue. It would therefore make sense not to combine the Selenium and Tellurium residue with the CPL residue and thus dilute the PGM content unnecessarily, but rather find a treatment route that would separate the PGMs from the unwanted elements contained in the CPL residue. The STR residue should then be treated separately.

In order to treat the CPL residue in-house and blend it with the primary feed material to the PMR – the FIC produced in the Magnetic Concentrator Plant – the total mass of the CPL residue needs to be reduced by at least 95% to make this option viable, as this would represent approximately 20% of the current FIC mass. The elements contained in the B residue therefore need to be minimised with regard to the PGMs. The major elements that would present problems in the PMR, if present in larger concentrations, would be Cu, Ni, Fe, Se, Te, Pb and Ag.

	SLR	***Period A***	***Period B***
Element	***Assay (g/t & %)***	***Assay (g/t & %)***	***Assay (g/t & %)***
Cu %	13.2	53.29	37.75
Ni %	3.1	1.57	1.5
Fe %	17.4	0.1	1.76
S %	15.5	37.1	57.25
Pt	125	45.2	105
Pd	536	819	2150
Rh	173	42.2	78
Au	75	108	287
Ru	398	47	128
Ir	-	14.9	35.4
Se	4049	1610	1793
Te	1167	170	302
Pb	2439	118	333
As	848	115	132
Sn	33	58.3	56
Mn	578	<0.02%	<0.02
Bi	285	6.56	14.7
Sb	202	55.5	89.5
Ag	615	-	-

Table 1: A comparison of current BMR and new BMR residues

Problem statement

It is clear from mass balances done on residues from initial test work that the following needs to be achieved in order to treat this residue in-house successfully:

(i) The final residue mass needs to be reduced by at least 95%.

(ii) The PGM losses must be minimal.

(iii) The extraction of Cu, Ni, Fe, S, Se, Te, Pb, Ag and SiO_2 needs to be such that residue concentrations meet the maximum limits specified by the PMR once this stream is combined with the current FIC.

From the literature search as well as preliminary scoping tests done for possible treatment routes, it is clear that a one-step hydrometallurgical process would not be able to accomplish this. A number of possible processes that could meet the above criteria were suggested following from the literature survey. It was evident that a copper pressure polishing leach would be required as a first step in the proposed process in order to extract as much of the copper, nickel and sulphur from this residue **(see B Period, Table 1)**. However, scoping tests using a similar residue revealed that there was too much elemental sulphur in the residue to successfully leach this and extract the copper and nickel sulphides. The B residue contains 36% elemental sulphur, which prevents the leaching of the base metals due to agglomeration of particles covered in a layer of molten (and subsequently re-solidified) elemental sulphur.

It was therefore decided to employ a caustic leach in order to leach as much of the elemental sulphur as possible before a sulphuric acid pressure leaching step can be used. The optimum process conditions then had to be established to limit the dissolution of the PGMs contained in the residue while maximising the extraction of elemental sulphur. This was done via a series of batch leaching tests with reasonable success, and optimum process conditions were determined. (See section 4)

After this was accomplished successfully, the A residue was treated via a caustic continuous leach under the optimal conditions determined from the batch leaching tests. (See section 5). The treated residue was then used as feed material in a series of sulphuric acid pressure leach tests in order to determine the most appropriate leaching conditions for this. The results are presented in section 6 .

This two-step process tested can be taken as the first two steps in the proposed process flow sheet, although additional steps are still required as Ag would still remain in the residue. Further development work is needed in terms of:

(i) dissolution of Ag
(ii) treatment of STR residue
(iii) handling the effluent stream.

SECTION 2

LITERATURE REVIEW

This literature review has focused on possible technologies and treatment routes involving similar elements and possibly similar mineralogy. From the literature reviewed, the possible treatment routes that could be employed in the existing Base Metal Refinery can be classified into four main types of processing routes. These are:

(i) Sulphuric acid leach processes
(ii) Caustic leach processes.
(iii) Chloride leach processes.
(iv) A combination of pyrometallurgical routes followed by hydrometallurgical options.

From the literature survey, it is evident that no single process will treat the whole suite of elements in the desired manner and cleanly separate out the PGMs. Having considered the capital cost of equipment, the application of the process on a small scale, the ease with which the process can be successfully implemented in the existing Base Metal Refinery, and the possible disadvantages and process-related problems of a pyrometallurgical route, it was decided to propose a study on a combination of a caustic leach / sulphuric acid leach process. The literature discussed will cover the following two possible processing routes.

- Caustic leach processes
- Sulphuric Acid Leach Processes

2.1 Sulphuric Acid Leach Processes

During the literature survey, various processes for leaching base metals were studied that used sulphuric acid as lixiviant. In the industry there are many applications where this medium is employed, and parameters and conditions vary considerably. This literature survey is a short summary of some applicable literature on the specific leach envisaged.

2.1.1 Separation of precious metals from the rest of the elements in copper sludge

In a European patent application by Thomas in 1982[4], a process is described in which the precious metals (gold and PGMs) present in a solution can be purified from nuisance elements such as Bi, Pb, Sn, As, Sb. The process involves treating the solution with SO_2 gas in the presence of halide ions and dissolved Se. This treatment selectively precipitates the precious metals and the Se, while the nuisance elements remain in solution. The first step in this process is to dissolve and extract copper and tellurium from anode sludge. The feed material composition was:

Element	***%***	***Element***	***%***	***Element***	***%***
Cu	8–30	***Ag***	7–14	***Bi***	0.2–0.7
Ni	4–10	***Au***	0.1–0.4	***Sn***	0.1–0.8
Se	7–20	***PGMs***	1–4	***SiO2***	0.4–50
Te	1–5	***Sb***	0.1–0.2	***As***	0.3–2
Pb	2–10				

Table 2: Feed composition of European patent

The process conditions were the following:

Temp : 105°C
pO_2 : 550 kPa air
Acid conc. : 180g/l H_2SO_4
Time : 5 hours

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O \quad (1)$$

$$Cu_2Se + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O + Se \quad (2)$$

$$Cu_2Te + 2H_2SO_4 + 2O_2 \rightarrow 2CuSO_4 + H_2O + H_2TeO_3 \quad (3)$$

Satisfactory extraction of copper and tellurium could be achieved in five hours at 105°C and 550 kPa using air, as higher oxygen concentrations tend to increase selenium extraction. The residue from this mild oxidative pressure leach is leached with chlorine to dissolve most of the metals and then to selectively reduce Se and PGMs with SO_2. The remaining tellurium is also reduced, and all reduced metals precipitate as solids.

$$Se + 4H_2O + 3Cl_2 \rightarrow H_2SeO_4 + 6HCl \qquad (4)$$

$$S + 4H_2O + 3Cl_2 \rightarrow H_2SO_4 + 6HCl \qquad (5)$$

$$Pt + 2HCl + 2Cl_2 \rightarrow H_2PtCl_6 \qquad (6)$$

$$Ag_2Se + 4Cl_2 + 4H_2O \rightarrow 2AgCl + 6HCl + H_2SeO_4 \qquad (7)$$

$$H_2SeO_4 + 2H_2O + 3SO_2 \rightarrow Se + 3H_2SO_4 \qquad (8)$$

$$H_2PtCl_6 + H_2SeO_4 + 6H_2O + 5SO_2 \rightarrow PtSe + 5H_2SO_4 + 6HCl \qquad (9)$$

This residue is then treated with a caustic oxidative pressure leach in order to selectively dissolve Se from the PGMs. This is filtered off and the tellurium and copper remaining in the residue are dissolved with dilute sulphuric acid at atmospheric conditions.

$$Na_2TeO_4 + H_2SO_4 \rightarrow H_2TeO_4 + Na_2SO_4 \qquad (10)$$

$$Cu(OH)_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O \qquad (11)$$

In the new BMR process, SO_2 will be used to reduce the envisaged Se/Te leached during the CPL leach.

Extraction results were:

Element	***% Extraction***	***Element***	***% Extraction***
Cu	97.5	***Pb***	0.7
Ni	13	***SiO2***	0.4
Se	5	***As***	48
Te	76.3	***Sb***	37.5
Bi	58.4	***Sn***	12.9
PGMs	8.3	***Ag***	0.02

Table 3: Extraction results of European patent application

2.1.2 Recovery of Te from leach liquor after H_2SO_4 leaching of copper sludge

In the different processes described by Hoffmann[3] and by Shibasaki[7], it might be possible to treat Cu and Te dissolved, first in a reactor with copper shot in order to remove Te by cementation, which would separate a large portion of the tellurium from the rest of the impurities. This is also very relevant if employing a sulphuric acid pressure leach on the CPL residue, whereby a large portion of the tellurium can be separated from the rest of the unwanted elements, thereby creating a possible value-added step in that tellurium metal can be recovered as a saleable product

$$H_2TeO_{3(aq)} + 2H_2SO_4 + 4Cu \rightarrow Cu_2Te + 2CuSO_4 + 3H_2O \qquad (12)$$

Tellurium metal is recovered from the copper telluride by slurrying it in a sodium hydroxide solution and sparging with air to form sodium telluride which can be removed from the copper stream and further treated. Alternatively, this copper telluride product can find a market as a master alloy for the production of free machining copper alloys.

2.1.3 Treatment of Se and Te residue

In a publication by Steenekamp and Dunn[19], a sulphuric acid leach at 145°C and 700kPa oxygen is employed on a sulphide residue and the indications are that most of the base metals are dissolved, as well as 80% of the Selenium and Tellurium. Data on exact process conditions and extraction results were however very limited in this paper.

$$Cu(OH)_2\ CuSO_4 + H_2SO_4 \rightarrow 2CuSO_4 + 4H_2O \qquad (13)$$

$$Cu_2S + H_2SO_4 + 2.5O_2 \rightarrow 2CuSO_4 + H_2O \qquad (14)$$

$$CuS + 2O_2 \rightarrow CuSO_4 \qquad (15)$$

$$5NiS + 2CuSO_4 \rightarrow Cu_2S + 2NiSO_4 + Ni_3S_4 \qquad (16)$$

$$NiS + 2O_2 \rightarrow NiSO_4 \qquad (17)$$

Then a selenium/tellurium removal step with SO_2 injection is used to precipitate selenium/tellurium as Cu_2Te & Cu_2Se. The copper selenide and telluride residue is repulped in sodium hydroxide liquor and leached at 50kPa total pressure at approximately 85°C in an oxygen containing atmosphere. This leach is repeated to remove in excess of 80% of the selenium and tellurium.

$$Cu_2Se + 2NaOH + 2O_2 + H_2O \rightarrow 2Cu(OH)_2 + Na_2SeO_3 \qquad (18)$$

$$Cu_2Te + 2NaOH + 2O_2 + H_2O \rightarrow 2Cu(OH)_2 + Na_2TeO_3 \qquad (19)$$

The filtrates are combined and neutralised with sulphuric acid, and then metalloids are precipitated with thiourea. High acid tenors are responsible for the solubilisation of certain PGMs. [18,19]

2.1.4 Leaching parameters varied during sulphide leaching

Research done by Shneerson and Lapin[20] showed that 98% of copper could be dissolved at 110°C and oxygen partial pressures of 400–600kPa. The concentrate (Cu = 65%, sulphur = 22%) can be leached with copper extraction completed within 6 hours. The main purpose of these studies was to find those conditions of the pressure acid leach that would ensure the maximum level of copper recovery into solution, the maximum level of sulphur transfer into elementary form and the minimum level of PGM dissolution into solution.

$$\mathrm{Cu_{1.8}S + 0.8H_2SO_4 + 0.8O_2 \rightarrow 0.8CuS + CuSO_4 + 0.8H_2O} \tag{20}$$

$$\mathrm{4.8CuS + 2.4CuSO_4 + 3.2H_2O \rightarrow 4Cu_{1.8}S + 3.2H_2SO_4} \tag{21}$$

$$\mathrm{CuS + H_2SO_4 + 0.5O_2 \rightarrow S^o + CuSO_4 + H_2O} \tag{22}$$

$$\mathrm{CuS + 2O_2 \rightarrow CuSO_4} \tag{23}$$

The conditions were the following:

Initial Acid	:	100 g/l	Temp	:	108°C
Terminal Acid	:	5–12g/l	Cu	:	35 g/l
Ni	:	14 g/l	Fe	:	2 g/l
L: S	:	9–11 to 1	O_2 kPa	:	400–600kPa
Time	:	6 hrs			

The following parameters were varied:

1. Initial copper and nickel concentrations
2. Oxygen partial pressure from 400–600kPa
3. Temperature from 108–140°C

The observations made showed that varying the initial copper and nickel concentrations in solution and varying the oxygen partial pressure had no significant effect on the final copper extraction (98–99%) if the test were run over a period of 6 hours; however, they do affect the rate of copper extraction.

Increasing the temperature led to an acceleration in copper extraction, but the rate of sulphide sulphur oxidation to elemental sulphur decreased. When the temperature was increased, more rhodium, ruthenium and iridium were also dissolved. The total losses of PGMs into solution were less than 0.3% of the total initial residue mass. At these conditions mentioned, the following dissolutions were showed:

Temp°C	*Time*	*V:S*	*% Cu Solution extraction*	*% S in cake*	*S→ So Recovery in solution*	*% solids in cake*
108	4	11	98.7	85.2	70.2	22
120	3	8.6	97.4	62.5	44.1	18
140	2	8.2	98.1	73.6	34.8	12

Table 4: Extraction results after varying temperatures

Pt & Pd	:	< detection limit
Rh	:	2% of initial content
Ru	:	20% of initial content

- Silver dissolution is minimal.
- No mention was made of selenium, tellurium or any other elements.
- The major mineralogical compounds were bornite (Cu_5FeS_4) and CuS.
- 80% sulphide sulphur was oxidised to S^o form and 20 % into solution as sulphate.

2.1.5 Process for maximum sulphide oxidation to sulphate

In test work for the Rustenburg BMR expansion project[27], the main objectives of the envisaged process were to leach as much of the base metals as possible. Additional objectives included minimal formation of elemental sulphur and minimal dissolution of the PGMs.

The copper and remaining nickel in the 3rd stage non-oxidising leach residue are leached to extinction in the 4th stage sulphuric acid copper pressure leach (CPL), and the sulphide sulphur is oxidised predominately to sulphate in the copper pressure leach with oxygen at elevated temperature and pressure. The major sulphide minerals in the CPL feed solids include djurleite, digenite, possibly anilite, polydymite and/or fletcherite. X-ray diffraction analysis of the NOX discharge solids from the continuous campaign confirmed the presence of chalcocite, digenite and polydymite, and also showed traces of vaesite (NiS_2). The solids also contained a small portion of the original iron (bornite), some of which is extracted in the CPL.

The initial stages of the oxidising leach involve primarily reaction of the cuprous copper sulphides and, since they are sulphur deficient, the necessary acid is supplied as the spent electrolyte.

$$Cu_2S + H_2SO_4 + 0.5\ O_2 \rightarrow CuS + CuSO_4 + H_2O \qquad (24)$$

$$Cu_9S_5 + 4H_2SO_4 + 2\ O_2 \rightarrow 5CuS + 4CuSO_4 + 4H_2O \qquad (25)$$

$$Cu_7S_4 + 3H_2SO_4 + 1.5\ O_2 \rightarrow 4CuS + 3CuSO_4 + 3H_2O \qquad (26)$$

$$Cu_5FeS_4 + 2H_2SO_4 + O_2 \rightarrow 3CuS + FeS + 2CuSO_4 + 2H_2O \qquad (27)$$

$$4NiS + H_2SO_4 + 0.5\ O_2 \rightarrow Ni_3S_4 + NiSO_4 + H_2O \qquad (28)$$

The next phase of the leach involves oxidation of the sulphide sulphur to sulphate and dissolution of the associated metals. The reaction equations for these are given below.

$$Ni_3S_4 + 7.5\ O_2 + H_2O \rightarrow 3NiSO_4 + H_2SO_4 \qquad (29)$$

$$CuNi_2S_4 + 7.5\ O_2 + H_2O \rightarrow 2NiSO_4 + CuSO_4 + H_2SO_4 \qquad (30)$$

$$FeS + 2O_2 \rightarrow FeSO_4 \qquad (31)$$

$$NiS + 2O_2 \rightarrow NiSO_4 \qquad (32)$$

$$CuS + 2O_2 \rightarrow CuSO_4 \qquad (33)$$

During the course of the leach, ferrous iron is oxidised to ferric and is subsequently reduced by reaction with the remaining sulphides, until these are essentially exhausted.

$$2FeSO_4 + 0.5\ O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (34)$$

Sufficient acid is provided to the CPL by way of the spent electrolyte, such that together with the acid formed by the reactions of polydymite (Ni_3S_4) and fletcherite ($CuNi_2S_4$), it meets the requirements of the initial reaction of the cuprous sulphides, and provides a terminal acidity of about 10 g/L.

An excessive addition of acid is detrimental, in that it will promote the formation of elemental sulphur which, in its molten state, will deter complete oxidation of the sulphides and, in extreme cases, may cause agglomeration of the sulphides. Reaction 35 will be promoted by excessive acid, lower temperatures and low oxygen availability.

$$\mathbf{CuS + 0.5\ O_2 + H_2SO_4 \rightarrow CuSO_4 + S° + H_2O} \qquad \mathbf{(35)}$$

Even with relatively low terminal acidities, small amounts of elemental sulphur were obtained in the CPL tests. Although the sulphur may have been formed from the reaction of covellite, another possibility could be that it may have been formed in reactions of the polydymite or fletcherite, as shown in reactions 36 and 37.

$$\mathbf{Ni_3S_4 + 6\ O_2 \rightarrow 3NiSO_4 + S°} \qquad \mathbf{(36)}$$

$$\mathbf{CuNi_2S_4 + 6\ O_2 \rightarrow CuSO_4 + 2NiSO_4 + S°} \qquad \mathbf{(37)}$$

The oxidation reaction equations above all show the oxygen reacting directly with the sulphides. In practice, the presence of a finite amount of iron (>0.5 g/L) as an oxygen transfer medium is desirable. An acid deficiency in CPL will still result in the reaction of the cuprous sulphides to covellite, but with precipitation of considerable copper as a basic copper sulphate, as illustrated in reaction 38 for chalcocite.

$$\mathbf{2Cu_2S + CuSO_4 + O_2 + 2H_2O \rightarrow 2CuS + CuSO_4{\cdot}2Cu(OH)_2} \qquad \mathbf{(38)}$$

Under these conditions, iron would be hydrolysed and precipitated from solution which, in turn, would have a deleterious effect on the leaching kinetics of covellite and the other sulphides. During the course of the leaching of the sulphides, a number of impurities, including arsenic, selenium and tellurium are also dissolved. Towards completion of the leach, as the solution oxidation potential increases, dissolution of the PGMs also occurs in the sequence ruthenium, rhodium, palladium and platinum.

Different elements and conditions

Base metals (Copper, Nickel, Iron)

The presence of molten S^o had a marked influence on Ni extractions, and only with additional time and $S^o \rightarrow SO_4^{2-}$ oxidation did Ni extractions improve. There was slower Nickel extraction kinetics with higher acid levels (100g/l), but after 4 hours, complete Ni extraction occurred. Even at high acid concentrations (>100g/l), elemental sulphur formation will be decomposed to sulphates over time. The target final acid concentration in the product liquor was about 10 g/L, which was considered to be sufficient to prevent precipitation of the dissolved iron during the leach. When the acid content is decreased, Ni extractions are quicker and $S^o \rightarrow SO_4^{2-}$ oxidation is also quicker, but appeared to be less complete.

The temperature and oxygen partial pressure had a mild effect on the initial nickel extraction rate, with 0.5 hours extractions ranging from 76.9% (140°C, 140 kPa oxygen partial pressure) to 99.5% (140°C, 540 kPa oxygen, as well as 150°C, 340 kPa oxygen). After one hour, however, the extraction of nickel in all of the tests was ≥ 99.4%.

The copper extraction kinetics were also affected by the oxygen pressure and the leach temperature, but to a greater extent than those of nickel. The mildest conditions (130°C, and 140°C/140 kPa oxygen) required a retention time of 3 hours to achieve 99% extraction, whereas all the other conditions achieved this within 2 hours.

	Ni	*Co*	*Cu*	*Fe*	*S*	*% Mass Loss*
CPL	99.7	99.2	98.1	65.1	93.8	96.9

Table 5: Final extractions of CPL Leach

It is noted that in a batch leach, complete oxidation of the elemental sulphur can be achieved with the additional retention time. Since the molten sulphur had impeded the leaching of the nickel sulphides to a considerably greater extent than of the copper sulphides, this would suggest that the elemental sulphur had come mainly from the nickel containing sulphides, such as fletcherite or polydymite.

Temperature increases the Cu extraction kinetics, but after 6 hours at 140°C, all Cu extractions were above 99%. Ni extractions were not influenced by temperature (130–150°C) after 4 hours. By increasing oxygen partial pressure at constant 140°C, a quicker and more complete extraction from 140kPa to 340kPa was achieved, but without much further difference when using 540kPa.

Sulphur

Lower acidity improves the rate of $S^o \rightarrow SO_4^{2-}$ oxidation. Sulphur oxidation was complete after 4 hours, even when varying the temperatures and pressures, but the lowest S^o yields appear to be in the milder conditions, ie 130/140kPa. (Refer to **Table 6** for results when varying the temperatures and pressures on elemental S formation.)

It is interesting to note that, based on the rate of decrease of the solids concentration, the initial leach rate at 140°C at the lowest of the three oxygen pressures was the slowest, but the solids contained the least elemental sulphur and the extent of leaching was eventually the highest. In a test, conducted at 130°C, the leaching rate was similarly slow and the solids also contained very little elemental sulphur. The lowest level of elemental sulphur formation occurs in the tests with the mildest conditions.

Elemental sulphur was observed in some of the samples in all of the tests. Although some of the low concentrations may be suspect, due to the method by which they were determined, some – as noted previously – were in the 28–32% range in the kinetic samples and the final residue values were in the 18–26% range. These values are provided in the summary Table 6.

The data suggest that the formation of elemental sulphur did not occur until virtually all of the nickel and most of the copper had been extracted. This would indicate that the elemental sulphur was formed during the leaching of covelite (CuS).

Series	***°C***	***Oxygen kPa***	***Test***	***Elemental Sulphur in Solids (Calculated), %***						
				0.5 h	***1 h***	***1.5 h***	***2 h***	***3 h***	***4 h***	***Final***
Temp	130	340	7	0	0	0	0	12	0.2	26
	140	340	6	0	0	9	13	11	0	26
	150	340	8	0	29	32	11	0	0	23
Press	140	140	9	0	0	0	0	3	8	18
	140	340	6	0	0	9	13	11	0	26
	140	540	10	0	0	30	28	8	0	25

Table 6: Elemental S formation by varying temperatures and pO_2

Selenium/Tellurium

This study indicated that selenates (Se (VI)) were initially dissolved and, as the oxidation of sulphides approached completion, the selenates were reduced or decomposed to selenite, in spite of increasing potentials (Refer to **Table 7** for Se concentration at varying temperatures and pO_2). Selenium extraction increases with higher acid concentrations. Increasing temperature showed increasing selenium concentration. At higher temperatures the conversion of Se (VI) to Se (IV) is quicker. At higher pressures, the conversion of Se (VI) to Se (IV) is quicker and more Se dissolves (total). Increasing the retention time has the effect that the conversion of Se (VI) to Se (IV) is more complete.

The STR feed solution contained about 75 mg/L Se (VI) and 100 mg/L Se (IV). Essentially all of the Se (IV) and about one third of the Se (VI) were removed from the solution in the STR circuit, leaving about 50 mg/L Se in the feed to electrowinning. What is noteworthy, is that the selenium in solution was all present as the selenate (Se (VI)) species until it reached its ultimate extraction, at which point the selenate was progressively decomposed and/or reduced to selenite (Se (IV)).

It has been reported that elevated temperatures (generally >160°C) will promote a decomposition of selenate to selenite, with a release of oxygen.

$$2H_2SeO_4 \rightarrow 2H_2SeO_3 + O_2 \qquad (39)$$

The fact that this apparently occurred in the CPL, under oxygen pressure and at a relatively high oxidation potential, however, is surprising. It is noted that in all of the CPL tests, a portion of the sulphide sulphur had been oxidised to elemental sulphur, which over an extended retention time, was at least partially further oxidised to sulphate. It would certainly be of interest to examine whether the behaviour and the change in speciation of the selenium were in any way related to the presence and oxidation of the elemental sulphur.

Series	°C	Oxygen kPa	Test	Selenium (total) Concentration, mg/L						
				0.5 h	***1 h***	***1.5 h***	***2 h***	***3 h***	***4 h***	***Final***
Temp	130	340	7	60.4	109.8	124.0	129.6	136.0	132.4	136.6
	140	340	6	98.6	138.2	151.8	155.4	150.0	151.5	151.3
	150	340	8	135.2	153.2	157.4	154.3	158.6	154.7	163.6
Press	140	140	9	41.4	105.4	136.4	146.0	147.6	147.1	146.8
	140	340	6	98.6	138.2	151.8	155.4	150.0	151.5	151.3
	140	540	10	123.0	169.8	167.2	171.6	170.8	172.3	175.3

Table 7: Selenium concentration by varying temperature & pO_2

The temperature and, especially, the oxygen partial pressure had a marked effect on the dissolution kinetics of selenium, with 0.5 hours concentrations ranging from 41–135 mg/L. By the time 99% copper extraction had been reached, the corresponding selenium concentrations were in the 136–167 mg/L range, and in most cases, had reached their ultimate levels. The final discharge concentrations ranged from 136–175 mg/L, and there was a definite correlation between these concentrations and the leach parameters, with the highest concentrations corresponding to the most aggressive leach conditions. During the course of each of the leach tests, the selenium, initially dissolved as Se (VI), was gradually converted to Se (IV). The conversion of Se (VI) to Se (IV) was essentially negligible until 98–99% of the copper had been extracted and the extraction of selenium had reached its ultimate levels. Consequently, the rates of conversion were affected by both the temperature and the oxygen pressure. Under milder leach conditions, the conversions were lower, in spite of having attained 99% copper extraction. At 140°C and the lowest oxygen partial pressure, the conversion was slightly lower, at almost 50%, but at the lowest temperature of 130°C, the conversion was less than 25%, which indicated that of the two parameters under investigation, the temperature had the greater effect on the Se (VI) to Se (IV) conversion.

The behaviour of selenium is particularly interesting. Common wisdom would expect the selenium to dissolve initially as the selenium (IV) and associated selenite species, and then progressively become oxidised to selenium (VI), or selenate, as the oxidation potential of the solution increases. In preceding studies for Anglo Platinum[11] in 2002, however, it was found that contrary to expectations, the selenium was initially dissolved as the selenate and as the oxidation of the sulphides approached completion, the selenate was reduced or decomposed to selenite, in spite of the increasing solution potentials. The selenium in the CPL liquor is present in both the selenite Se (IV) and selenate Se (VI) anionic states, with the relative proportions depending on the conditions of the CPL.

Tellurium shared a slight correlation with acid concentration, meaning the higher the acid concentration, the higher the tellurium concentration. It appears as if Te concentration decreases with residence time under the above conditions. Increasing oxygen partial pressures showed increasing tellurium concentrations. Tellurium concentrations generally increased with time, up to about 1.0 hour, and then decreased, to the 0.3–7.6 mg/L range, and showed a slight correlation with acid concentration. Usually, this type of behaviour would be associated with the oxidation and hydrolytic precipitation of iron, but the total iron concentrations were relatively low (0.5–0.7 g/L) and, on a macro scale, there did not appear to be any precipitation of iron. Also, the amount of iron accounted for by the iron content of the final solids – some of which may have been leached and subsequently precipitated – corresponded to only between 15 and 50 mg/L.

PGMs

As the leach nears completion, the oxidation potential increases and Ru (360mV) > Rh (490mV)>Pd (540mV)>Pt dissolution occurs (Ag/ AgCl electrode). Rh dissolution in the batch tests (140°C, 45g/l acid, and 340kpa/600kPa) was 0.2–0.3 ppm, Ru 2.3 ppm. Rh concentration does not appear to be affected by Temp/ Pressure. Ru appears to be affected by both parameters and the mildest conditions is the best. Pt/Pd concentrations were below the detection limit.

Rhodium solution profiles show between 0.5–1.1 mg/L at 0.5 hours, increasing to 0.88–1.08 mg/L by 2 hrs and largely remaining there for the remainder of the test. There was no clear indication of any temperature or pressure effects on the final levels. Ruthenium profiles show a dependence of the dissolution kinetics on both temperature and oxygen pressure. The concentrations at 2 hours ranged from 2.7–3.5 mg/L, and were the lowest in the test at 140°C, at the lowest oxygen pressure, followed by the test at 130°C, i.e., the mildest conditions.

2.1.6 Role of oxygen and ferric in sulphide oxidation

In test work conducted by Hofirek & Frampton[28] in search of an improved metallic concentrate leaching rate, the following were found:

$$CuS + 2O_2 \rightarrow CuSO_4 \quad (40)$$

$$NiS + 2O_2 \rightarrow NiSO_4 \quad (41)$$

During the course of the leach, ferrous iron is oxidised to ferric and is subsequently reduced by reaction with the remaining sulphides, until these are essentially exhausted.

$$2FeSO_4 + 0.5\ O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (42)$$

$$Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe_2O_3 + 3H_2SO_4 \quad (43)$$

$$4Fe_2(SO_4)_3 + CuS + 4H_2O \rightarrow 8FeSO_4 + CuSO_4 + 4H_2SO_4 \quad (44)$$

There are strong indications that iron plays a pivotal role in the oxidation of covelite. In the absence of Fe in solution, covelite dissolution rate is at least an order of magnitude slower, possibly due to very slow kinetics of the direct sulphide oxidation by dissolved oxygen. Acid concentration also controls the iron level in solution, and in this way, will control **Reaction 42**. It is thought that soluble iron acts as an electron carrier transporting electrons from metals and sulphur to dissolved oxygen in a cyclical manner. Total salt concentration can affect leaching rate, because it affects the rate of oxygen mass transfer from gas to liquid phase due to decreased oxygen solubility, but it also slows down diffusion of the oxidant, either ferric ion or oxygen, to the sulphide particle. It is well known that a dilution of the mix considerably speeds up the rate of oxygen uptake. There are numerous articles on CuS oxidation, and from this it appears to be directly proportional to the oxygen partial pressure. This ensues from the fact that oxygen mass transfer from the gaseous to the liquid phase is a rate controlling step. The rate of oxygen mass transfer is directly proportional to the oxygen concentration between the gas and liquid phase, the value of which is fixed by the degree of oxygen enrichment, on the assumption that the concentration in the liquid phase remains constant at constant temperature and pressure. In layman's terms, doubling the oxygen concentration in the gas input, will double the leaching rate and halve the leaching time provided that all other variables are kept constant.

Hofirek[21] did a test campaign on similar residues, and it is noted that when insufficient excess of acid is used, iron readily precipitates from solution in the form of basic sulphates or oxides. In this document, the relationship between ruthenium and rhodium solubility and the total ferric concentration terminated in the potential range of 480–515mV SCE at 140°C and 490–525mV SCE at 150°C is described. An increase in the solubility of both metals with increasing Fe concentration is apparent. It is well known that Fe precipitate acts as a good collector for soluble PGMs. Low Fe concentration appear to have a marked effect on Pd solubility. Despite potentials close to 600mV SCE, Pd dissolution <0.1% was observed. It is also shown that with this residue, indications are that leaching above 520mV SCE is wasteful increasing PGM dissolution only. At varying temperatures, PGM solubilities showed a peak, surprisingly, at temperatures of 140°C, and it seems that appreciable PGM dissolution takes place predominantly during the sulphides leach, which is in the 350–460mV redox potential range.

$$2FeSO4 + 0.5\ O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (45)$$

$$Fe_2(SO_4)_3 + H_2O \rightarrow Fe_2O_3 + H_2SO_4 \qquad (46)$$

$$4Fe_2(SO_4)_3 + CuS + 4H_2O \rightarrow 8FeSO_4 + CuSO_4 + 4H_2SO_4 \qquad (47)$$

Reaction 47 does not appear to take place below 130°C prior to a redox potential of 500mV. This reaction controls the rate of redox change, which, in the absence of an active reducing agent is fast, resulting in a short reaction time to reach a redox of 460mV despite low base metal extraction.

At 140°C, the dissolution of sulphides, although almost complete in the redox range 350–60mV, is relatively slow. The period of PGM attack is prolonged, resulting in appreciable PGM final concentration despite the moderate rate of PGM dissolution.

At 150°C, the sulphide dissolution is accomplished in a relatively short space of time, which then compensates for the higher rate of PGM dissolution. Also, the solubility of Fe decreases with increasing temperature, with further positive effect on PGM dissolution. It is common knowledge that ferric ion is hydrolysed in acidic solutions at elevated temperatures, and it precipitates in different forms. Final acidity and leaching temperature are the most important factors controlling the final iron concentration. It appears that above 35g/l acid, no Fe is precipitated at 140°C, whereas at 150°C, the limiting acid concentration is 50g/l. The leaching rate increases with increasing acidity particularly at a 140°C. The increased Fe concentration is the major contributor, although it is known that acidity itself promotes the oxidation of CuS. The leaching rate increases with increasing temperature and decreases with increasing sulphur content. Lower Fe concentration due to precipitation will lead to lower oxidation activity of the solution due to the lower iron concentration. Above a redox potential of 400–450mV (Ag/AgCl), the dissolution of monosulphides are the major reactions. The 150°C temperature maintained during this phase favours the direct oxidation of sulphides to sulphates.

$$\mathbf{CuS + 2\ O2 \rightarrow CuSO4} \qquad \mathbf{(48)}$$

$$\mathbf{NiS + 2\ O2 \rightarrow NiSO4} \qquad \mathbf{(49)}$$

When the redox potential rises to 500–510mV, the slope of the increase and the duration of the sulphide leach are dependant on the acidity and the Fe concentration in solution. Above a redox of 510mV usually more than 95% of the sulphides have been leached. The remaining ferrous in the absence of a reducing agent is rapidly oxidised to ferric which results in a sudden potential jump to 540–570mV. Earlier in this document reference was made to Warren[29], who stated that CuS dissolution rate is controlled by temperature and oxygen partial pressure and acid concentration and that it rapidly increases with an increase in all three parameters. Reference was also made to Biswas[30], who, on studying the dissolution of synthetic CuS, found that there was an increase in the leaching rate with increasing acidity to a level of 100g/l, followed by a decrease at higher acid concentrations. This he ascribed to reduced oxygen solubility in solutions with 100g/l acid. He suggested that up to an initial acid concentration of 98g/l, the reaction rate is controlled by the diffusion of protons through the sulphur film to the CuS/S interface. Hofirek referred to Gerlach[31], who found that even small ferric ion concentrations have a considerable effect on the leaching rate of CuS. Dobrokhotov[32] in the study of the pressure oxidation of base metal monosulphides in the presence of Fe and suggested the following mechanism.

$$\mathbf{MeS \rightarrow MeS_{act} \rightarrow Me^{2+} + S^{2-}}$$

$$\mathbf{2Fe^{3+} + S^{2-} \rightarrow S^0 + 2Fe^{2+}} \quad \mathbf{(50)}$$

$$\mathbf{6Fe^{3+} + S^0 + 4H_2O \rightarrow 6Fe^{2+} + 8H^+ + SO_4^{2-}} \quad \mathbf{(51)}$$

$$\mathbf{8Fe^{3+} + S^{2-} + 4H_2O \rightarrow 8Fe^{2+} + 8H^+ + SO_4^{2-}} \quad \mathbf{(52)}$$

$$\mathbf{4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O} \quad \mathbf{(53)}$$

Thermodynamic analysis of the above reactions shows that high acidity, low temperature and low oxygen partial pressure favour **Reaction (50)**, whereas decreasing acidity and increasing temperature and oxygen partial pressure, will shift the reaction mechanism in favour of the direct oxidation of sulphide ion to sulphate ion **(Reaction 52)**. In the MEC pressure leach, it has been found that no appreciable amount of elemental sulphur is formed at temperatures of 140–150°C, oxygen partial pressures of 120–200kPa and acid concentrations of up to 100g/l, whereas at 130°C, an acid concentration > 70g/l results in dominant formation of elemental sulphur, whilst at 50g/l acid the sulphate ion is the major product.

In another test work campaign by Hofirek[22], which was conducted on the residues of the above leach, the optimum conditions were found to be:

Leach temp	:	140°C	Pressure	:	1035kPa
Acidity	:	30–50g/l	Terminal redox	:	500mV SCE

Comparison of ALR vs. CPL residue vs. NaOH leach residue			
Element	***% composition***		
Cu	21.9	53	61
Ni	7.7	1.6	2
Fe	7.9	0.1	0.18
S	6.8	37	25

Table 8: Comparison of residues with Atmospheric leach residue in MCP

Chemistry

Redox potential < 440mV (Ag/AgCl)

$$\mathbf{CuS + 0.5\ O_2 + H_2SO_4 \rightarrow CuSO_4 + S^\circ + H_2O} \qquad (54)$$

Redox potential ≤ 440mV (Ag/AgCl)

$$\mathbf{NiS + 2O_2 \rightarrow NiSO_4} \qquad (55)$$

$$\mathbf{FeS + 2O_2 \rightarrow FeSO_4} \qquad (56)$$

Redox potential 440–490mV (Ag/AgCl)

$$\mathbf{CuS + 2O_2 \rightarrow CuSO_4} \qquad (57)$$

The major findings of this test work were the following:

1 Ni extraction appears to be significantly affected by temperature and initial acid concentration.

2 Reducing the initial acidity to 25g/l reduced PGM dissolution, however, BM dissolution was also depressed.

3 Major copper components are CuS and CuO. Copper sulphide commences in the redox range 430–450mv.

4 Sulphur extraction appears to be significantly affected by temperatures below 140°C. When all the BM are extracted, elemental sulphur is oxidised to sulphate.

Referring to **Table 8**, a comparison was done between residues to see the difference in content regarding the pressure leaching of the atmospheric leach in the MCP.

2.1.7 Some notes on sulphur chemistry

There are two forms of stable crystalline sulphur.

Orthorhombic Sulphur	Sα	Stable to 95.5°C.
Monoclinic Sulphur	Sβ	Stable above 95.5°C

Monoclinic Sulphur melts at 119.3°C.

If sulphur is heated rapidly and does not convert from orthorhombic to monoclinic, then orthorhombic sulphur melts at 112.8°C. Between 119.3 and 159°C, sulphur becomes molten and highly fluid; above 159 °C, it becomes highly viscous **(See Figure 3)**. This is due to the breakdown of the 8-ring structure of sulphur and the formation of sulfenyl diradicals. These sulfenyl diradicals attack other sulphur rings initiating polymerisation.

Habashi & Bauer studied the oxidation of elemental sulphur under the temperature range 60–170 °C,

$$S + 3/2\ O_2 + H_2O \rightarrow H_2SO_4 \qquad (58)$$

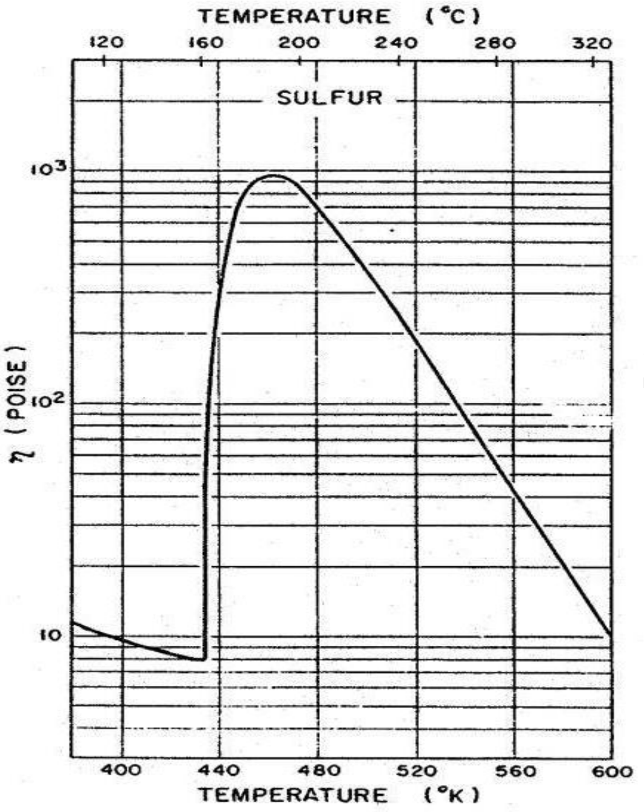
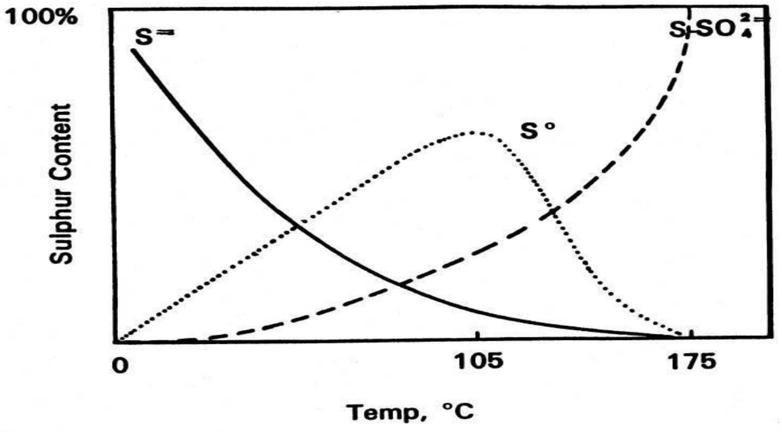


Figure 3: Viscosity of sulphur at varying temperatures[35]

The above reaction depends largely on temperature and oxygen pressure. The rates were only appreciable above the sulphur melting point (119°C) and then increased with increasing temperature. The initial acidity had practically no effect on the oxidation rate and the rate was proportional to the oxygen partial pressure and the following mechanism was proposed.

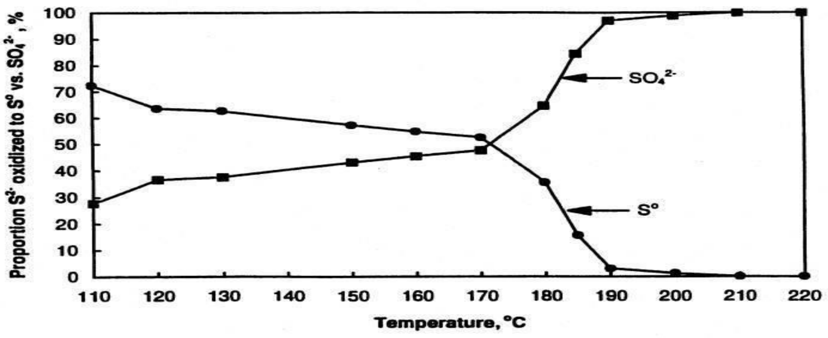
$$S + 3/2\ O_2 \rightarrow SO_3 \qquad (59)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (60)$$



Oxydation of sulphides at pH≤3
(From Metallurgical Reviews 1966 vol. II, p. 143)

Figure 4: Oxidation of sulphides at various temperatures[35]



Effect of Temperature on Relative Proportion of Sulphur Oxidized to S° vs SO$_4^{2-}$;
Oxidative Pressure Leaching of Gibraltar Copper Concentrate

Feed: 28.3% Cu, 28.0% Fe, 32.6% S
Conditions: 100 g/L concentrate, 690 kPa oxygen, 3 h

Hackl et al, COPPER 95, Vol III, pp. 559-577

Figure 5: Effect of temperature on type of sulphur formation[36]

2.1.8 *Summary of sulphuric acid leaching literature survey*

Base metals and sulphur

1 Test work conducted by varying the temperature around the sulphur melting point showed that it does not have a major impact on copper extraction, but that higher temperature leads to an acceleration of copper extraction. However, it has a major impact on sulphur oxidation, in that only 30% of sulphur gets oxidised to sulphate at

the lower temperatures, while at the higher temperatures almost 70% was oxidised to the sulphate form.

2 Excessive amounts of acid addition are detrimental in that they promote the formation of elemental sulphur which, in its molten state, will deter complete oxidation of the sulphides and, in extreme cases, may cause agglomeration of the sulphides. This will be promoted by excessive acid, lower temperatures and low oxygen availability.

3 An acid deficiency will still result in reaction of the cuprous sulphides to covelite, but with precipitation of considerable copper as a basic copper sulphate. Under these conditions, iron will also be hydrolysed and precipitated from solution which, in turn, would have a deleterious effect on the leaching kinetics of covelite and the other sulphides.

4 The presence of molten S^o had a marked influence on Ni extractions, and only with additional time and $S^o \rightarrow SO_4^{2-}$ oxidation did Ni extractions improve. There were slower nickel extraction kinetics with higher acid levels (100g/l), but after 4 hours complete Ni extraction occurred. Even at high acid concentrations (>100g/l), elemental sulphur formation will be decomposed to sulphates with increasing time.

5 The lowest level of elemental sulphur formation occurred in the tests with the mildest conditions above the melting point of sulphur.

6 In the absence of Fe in solution, the covelite dissolution rate is at least an order of magnitude slower, possibly due to very slow kinetics of the direct sulphide oxidation by dissolved oxygen.

Selenium and tellurium

1 When oxygen is used in sulphuric acid pressure leaching, it increases the extraction of selenium.

2 At temperatures of 140^oC and 600kPa oxygen partial pressure, selenates (SeVI) are initially dissolved and, as the oxidation of sulphides approach completion, the selenates are reduced or decomposed to selenite, in spite of increasing potentials.

3 Selenium extraction increases with higher acid concentrations.

4 Increasing temperature showed increasing selenium concentration in solution. At higher temperatures, the conversion of Se (VI) to Se (IV) is more rapid.

5 At higher pressures, the conversion of Se (VI) to Se (IV) is more rapid, and more Se dissolves in total.

6 Increasing the retention time has the effect that the conversion of Se (VI) to Se (IV) is more complete.

7 The higher the acid concentration, the higher the tellurium concentration.

8 It appears as if Te concentration decreases with residence time.

9 Increasing oxygen partial pressures showed increasing Tellurium concentrations.

PGM leaching

1 High acid tenors are responsible for the solubilisation of certain PGMs.

2 Rh concentration does not appear to be affected by temperature/ pressure. Ru appears to be affected by both parameters and the mildest conditions are the best.

3 An increase in the solubility of Rh and Ru with increasing Fe concentration is apparent.

4 Decreasing the initial acidity will lead to a reduction in PGM dissolution.

2.2 Caustic Leach Processes

The main reasons for investigating a caustic leach as a possible treatment route for the copper pressure leach residue (CPL) are the following:

(i) Treatment of the complete residue and leaching of as much of the major base metals (Cu/Ni/Fe) as possible, as well as removal of amphoterics and other trace elements and separation of this from the PGMs in the residue.
(ii) Pre-treatment of the CPL residue for the removal of elemental sulphur.
(iii) Possible separation step between Se and Te.
(iv) Removal of as much of the amphoterics and other trace elements, before or after the CPL residue are leached in a sulphuric acid pressure leach.

The caustic pressure leach processes will leach sulphur compounds, selenium, arsenic and silica to various extents, depending on conditions. This could be used to separate most of the above elements from the PGMs, because indications are that if performed under certain conditions, caustic leaching will keep PGM dissolution to a minimum. Although a NaOH leach will separate some of the elements present in the CPL residue, it should not solubilise any of the lead, silver or tellurium and these elements are problematic in the current PGM refinery and must be removed as lead and silver would interfere in the current PGM separation process. Therefore, the main aim of investigating a possible caustic leach for treating, or pre treatment, of the copper pressure leach residue, is to remove as much of the unwanted elements, ie elemental sulphur, selenium, tellurium, lead, arsenic, tin, bismuth, antimony, silica, zinc, while minimising the dissolution of the PGMs.

In order to leach the CPL residue, elemental sulphur in the residue (35–55%) needs to be removed as was indicated by the scoping tests done on the current Primary Leach residue (PLR). In performing this leach under the conditions which were thought to be the ideal, a lot of sulphur balls were generated and this prevented extraction of the major base metal elements (Cu, Ni, Fe).

2.2.1 NaOH pressure leaching on a similar residue and NaOH atmospheric leaching on a Se and Te residue

In studies conducted by Dunn [11], the objective was to remove amphoteric elements (S, Se, As, Si), from a copper pressure leach residue. NaOH leaching was done under different conditions during this study, ie pressure as well as atmospheric conditions and with two different types of residues.

The aim of the caustic pressure leach was to dissolve amphoterics and impurities from the CPL residue, while leaving the PGMs and base metals in the residue. The aim of the caustic atmospheric leach was to dissolve Se and Te from the selenium and tellurium removal residue, which were precipitated with SO_2.

The residue treated during the NaOH pressure leach was a copper pressure leach residue, with high PGM content as shown in **Table 9**.

	Pt %	*Pd%*	*Au%*	*Rh%*	*Ir%*	*Ru%*	*Ag ppm*
CPL head	43.7	13.2	1.1	1.6	1.7	3.7	16628
	Se ppm	***Te ppm***	***Pb ppm***	***Si %***	***Cu %***	***Ni %***	***Fe %***
CPL head	31675	8482	12777	1.8	2.1	5.9	2.0
	S %						
CPL head	1.1						

Table 9: CPL initial residue for treatment in a NaOH pressure leach

The residue treated during the NaOH atmospheric leach was a selenium and tellurium residue as shown in **Table 10**.

	Pt ppm	*Pd ppm*	*Au ppm*	*Rh ppm*	*Ir ppm*	*Ru ppm*	*Ag ppm*
STR head	49	302	45	228	12	249	717
	Se ppm	***Te ppm***	***Pb ppm***	***Si %***	***Cu %***	***Ni %***	***Fe %***
STR head	20117	75	1990	na	15.4	3.7	0.6
	S %						
STR head	11.6						

Table 10: STR initial residue for treatment in a NaOH atmospheric leach

Process conditions

Pressure leach

Temperature : 150–210^{o}C
Oxygen Partial Pressure : 600–1 000kPa
NaOH concentration : 4–10g/l
Reaction time : 6hrs

Atmospheric leach

Temperature : 80^{o}C
Oxygen Partial Pressure : 60kPa
NaOH concentration : pH 8–12
Reaction time : 2hrs

Process chemistry

$$2SiO_2 + 4NaOH + O_2 \rightarrow 2Na_2SiO_4 + 2H_2O \quad (61)$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \quad (62)$$

$$\mathrm{CuS + 2O_2 + 2NaOH \rightarrow Cu(OH)_2(s) + Na_2SO_4} \tag{63}$$

$$\mathrm{NiS + 2O_2 + 2NaOH \rightarrow Ni(OH)_2(s) + Na_2SO_4} \tag{64}$$

$$\mathrm{FeS + O_2 + 6NaOH \rightarrow 2Fe(OH)_3(aq) + 3Na_2SO_4} \tag{65}$$

$$\mathrm{2Se + 4NaOH + 3O_2 \rightarrow 2Na_2SeO_4 + 2H_2O} \tag{66}$$

$$\mathrm{2Te + 4NaOH + 3O_2 \rightarrow 2Na_2TeO_4 + H_2O} \tag{67}$$

Discussion

Pt %	*Pd%*	*Au%*	*Rh%*	*Ir%*	*Ru%*	*Ag %*	*S %*
< 0.001	< 0.001	<0.01	<0.01	<0.01	2.4	<0.01	>95
Se %	***Te %***	***Pb%***	***Si %***	***Cu %***	***Ni %***	***Fe %***	
>80	<0.01	<0.01	20	40	70	60	

Table 11: Extraction results during NaOH pressure leach using CPL residue

The caustic pressure leach resulted in a higher than 80% removal of Se and As and 96% removal of S_{tot}. but Te removal was minimal (<0.01%). Unexpectedly, Cu (40%), Ni (77%) and Fe (63%) also leached instead of precipitating as base metal hydroxides. Silica removal varied to a maximum of 20%.

Pt %	*Pd%*	*Au%*	*Rh%*	*Ir%*	*Ru%*	*Ag %*	*S %*
35.2	0.1	na	0.04	1.5	0.13	na	>93
Se %	***Te %***	***Pb%***	***Si %***	***Cu %***	***Ni %***	***Fe %***	
65	1.9	na	na	na	na	na	

Table 12: Extraction results atmospheric leach

The caustic atmospheric leach resulted in very little Te dissolution and only increased to 15% when a two-step leach with intermediate filtration was attempted. Se removal was between 60–70% and 90% of the S was removed. The dissolution of Pt increased as the NaOH concentration and temperature increased – up to 35% Pt dissolution at 80°C. At 50°C, the Pt dissolution was 0.2%.

The treatment of the caustic effluent entailed a boil-down before H_2SO_4, $CuSO_4$, $FeSO_4$ and thiourea were added to reduce elements in solution. Burnt lime (CaO) was added to precipitate metal ions and trace elements in a residue that was safe for disposal but any valuable metals in this residue would be lost. A major concern with caustic leaches is the dissolution of PGMs and base metals in the atmospheric and pressure leaches respectively, although the atmospheric caustic leach conditions can be adjusted (lower temperature and NaOH concentration) to minimise PGM dissolution. The pressure leach did not remove Te, Pb or Bi and only 10–20% of Si.

2.2.2 NaOH atmospheric leach with no oxygen input on a high PGM content residue

In a study conducted by Rivett, Mracek and Robinson[10], the objective was to leach a final PMR feed concentrate with extremely high silica content that is occasionally produced. The silica content creates filtration problems in the downstream process and needs to be removed from this concentrate residue.

Process conditions

Temperature	: 80°C
No Oxygen input	
NaOH concentration	: 2M
Reaction time	: 2 hrs

Under these conditions silica is dissolved with a high efficiency **(see Table 13)** as well as elemental sulphur. PGM dissolution was very limited and base metal extraction was not reported on.

	Pt %	***Pd %***	***Au %***	***Rh %***	***Ir %***	***Ru %***	***SiO_2 %***
Residue	99.9	99.5	99.9	100	99.5	100	20.4
Solution	0.1	0.5	0.1	0	0.5	0	79.6

Table 13: Extraction results on a NaOH leach on final concentrate with high PGM content

2.2.3 NaOH leaching in a high NaOH concentration performed under high pressure and temperature conditions

A variety of research experiments have been performed on the oxidation of slimes under pressure in an alkaline media. The general conditions, as stipulated by the Hoffmann[1]**,** were:

Process conditions

Temperature	: 200°C
Oxygen partial pressures	: 200–2 000 kPa
NaOH concentration	: 100–500 g/l
Reaction time	: 4–12 hrs

Process chemistry

$$Se(s) + 2NaOH\ (aq) + 3/2O_2 \rightarrow Na_2SeO_4 + H_2O \tag{68}$$

Under these conditions, the conversion of selenium and tellurium to the hexavalent state is substantially complete. The advantage of this is the separation of tellurium from selenium, as tellurium is insoluble in strongly alkaline media. Lead sulphate will be converted to lead plumbate (hydroxy complexes) and silica present will convert to sodium silicate. However, in this document, no reference is made to other elements present in a copper slime. The advantage of employing a NaOH leach is that it is done in a substantially non-corrosive medium. Also, compared to a pyrometallurgical process, there are no volatile Se losses and therefore no need for an expensive gas scrubbing circuit. The separation of Se and Te is normally difficult to achieve and employing a NaOH leach under the abovementioned conditions would result in a very good separation technique, simply because sodium tellurate is insoluble in a leach done in high NaOH concentrations.

The major disadvantage, however, is that all Se is converted to the hexavalent form, which makes its recovery very tedious.

2.2.4 NaOH leaching in a high NaOH concentration performed under atmospheric conditions without oxygen

Research was done by Orhan[2] on the treatment of EAF dusts by an alkaline caustic leach for the recovery of zinc and lead under the following conditions:

EAF dust composition			
Element	***% composition***		
Cu	0.24	***Pb***	3.05
Zn	33	***SiO_2***	3.15
Fe	26	***S***	trace

Table 14: EAF dust composition tested in a NaOH leach

Conditions

Temperature : Varied 25–95°C

No Oxygen

NaOH concentration : Varied 2–12M

Reaction time : 2 hrs

Solid: Liquid ratio : 1/7

Process chemistry

$$ZnO + 2NaOH + H_2O \rightarrow Na_2Zn(OH)_4(aq) \quad (69)$$

$$PbO + 2NaOH + H_2O \rightarrow Na_2Pb(OH)_4(aq) \quad (70)$$

$$2Na_2ZnO_2 + 2H2O \rightarrow 2Zn + 4\ NaOH + O_2 \quad (71)$$

Zinc and lead are selectively dissolved in sodium hydroxide, rejecting iron in the residue. From the caustic leach, copper solubility is low, while iron and calcium do not dissolve. The optimum conditions for the recovery of Zn and Pb via alkaline leaching are 10M NaOH, 1/7 S/L ratio, 95°C and 2 hours leaching. This paper is only of relevance if the components can be converted to the oxide form, possibly via a pyrometallurgical route before the hydromet treatment. This is a possible treatment option which could be considered, but was not during this study.

Results of EAF dust leaching testwork % composition		
Element	***25°C***	***95°C***
Cu	12	18
Zn	32	85
Fe	0.01	0.01
Pb	27	90

Table 15: Results of leaching EAF dusts in a NaOH medium

2.2.5 NaOH leaching performed under atmospheric conditions without oxygen

In a patent for the treatment of smelter flue dust from copper and lead smelters (Stoll[24]), the aim was to leach sulphur, lead and arsenic, and recover bismuth. The process conditions were as follows:

Process conditions

Temperature : Varied 50–100°C
No Oxygen
NaOH concentration : 2M
Reaction time : 20 minutes

The composition of flue dust from a copper and lead smelting process was:

Element	FD A Wt%	FD B Wt%
Cu	11	14
Fe	9	3
Bi	2.4	1.2
As	5.5	10
Pb	23	15
Mo	0.25	1.5
Sb	0.28	0.25
SiO2	3.1	2
Au(g/t)	3.75	2.81
Ag(g/t)	271	172
S	7.9	11

Table 16: Flue dust composition

The dusts occur as base metal sulphates, oxides, arsenates, and molybdates. Selective leaching can be performed in two stages. In stage 1, a slurry of dust and water, containing about 10–50% by weight of dust in a NaOH solution at pH 9.8 and at ambient temperature, selectively leaches out only sulphur, and lead and zinc are fairly insoluble under these conditions. This is referred to as a neutralisation leach.

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2(s) + Na_2SO_4 \quad (72)$$

$$PbSO_4 + 2NaOH \rightarrow Pb(OH)_2(s) + Na_2SO_4 \quad (73)$$

The extraction of sulphur was tested under various conditions and the following conclusions were drawn. As the pulp density decreased, the extraction of sulphur increased; this was probably due to the solubility of the sodium sulphate ion. As the leach time increased, the extraction of sulphur increased. Temperature had a negligible effect on sulphur extraction, which was between 60–80%.

After filtering the solution following sulphur removal, selective alkaline leaching in stage 2 exploits the differences in the relative stability of the various oxyanions in concentrated NaOH solutions. The caustic concentration is approximately 2M (80g/l) and leaching was conducted at a temperature of about 80–100^{o}C. Soluble oxyanions of Pb, Zn, Sn, Mo, As, Sb and sulphate dissolved, but elements such as copper, iron and bismuth exist as hydroxides under these conditions. Gold and silver are not be oxidised and stay in their stable metallic state. The test work showed that the ratio (gram NaOH/ gram flue dust) has a huge impact on the extraction of As, Cu, Mo, Pb and Zn.

This process also provides the opportunity to remove lead, based on the differential solubility of the oxyanions of lead. When lead is in the Pb (II) form, it exists as $HPbO_2^-$ ion in concentrated caustic solution, but if oxidised to Pb (IV) form, its solubility is significantly reduced.

$$Pb(OH)_2(s) + OH^- \rightarrow HPbO_2^- + H_2O \qquad (74)$$

$$Zn(OH)_2(s) + 2OH^- \rightarrow ZnO_2 + 2H_2O \qquad (75)$$

$$Pb_3(AsO_4)_2(s) + 9OH^- \rightarrow 3HPbO_2^- + 2AsO_4^{3-} + 3H_2O \qquad (76)$$

$$Cu_3(AsO_4)_2(s) + 6OH^- \rightarrow 3\ Cu(OH)_2 + 2AsO_4^{3-} \qquad (77)$$

The tests revealed that lead oxide solubilised at high hydroxide concentrations and is stable as the $HPbO_2^-$ ion, and that zinc, arsenic and molybdenum are all soluble at the high concentrations of NaOH. Copper and iron are stable and insoluble as hydroxides. Variables were tested for the high concentration caustic leach and the following was found:

At a temperature of 80^{o}C, the maximum lead and arsenic extractions were accomplished and extraction of every element increased as the caustic concentration was increased

Element	*% Extraction*
Bi	0
As	95.7
Cu	2.56
Fe	0.08
Mo	96.7
Pb	76
Zn	80

Table 17: Extraction results on Flue dust with a NaOH leach

The results in **Table 17** were achieved at a recommended 1.07 g NaOH/ g dust.

2.2.6 NaOH leaching performed under atmospheric conditions with oxygen on a Se and Te residue

Steenekamp & Dunn[19], showed that Te and Se can be leached selectively from a copper selenide and copper telluride precipitate, leaving the PGMs as part of the residue. The treatment consists of two leaches, the first to leach out tellurium and the second the selenium. The approximate leach conditions were as follows:

Conditions

Temperature : 80 °C
Pressure : 65 kPa
Time : 15–20 minutes
NaOH : 20 g/l

The leach is done in an autoclave under slight oxygen pressure conditions

$$\mathbf{Cu_2Te + 2O_2 + 2NaOH \rightarrow Na_2TeO_3 + 2CuO + H_2O} \quad \mathbf{(78)}$$

It is important to terminate the leach after the exact time given, because if leaching for longer, the telluride oxidises further to form a tellurate and re-precipitates to form a very difficult-to-dissolve precipitate. It is also important to discharge and filter immediately to prevent oxidation of the tellurite.

After filtration, the press is cleaned and the solids re-pulped. It is pumped back to the autoclave for a second leach to dissolve the selenium. The exact leaching conditions for the selenium leach are unfortunately not shown in this paper.

$$\mathrm{Cu_2Se + 2O_2 + 2NaOH \rightarrow Na_2SeO_3 + 2CuO + H_2O} \qquad (79)$$

Alternative reactions

$$\mathrm{Cu_2Se(s) + 2NaOH + 2O_2 + H_2O \rightarrow Na_2SeO_3 + 2Cu(OH)_2} \qquad (80)$$

$$\mathrm{Cu_2Te(s) + 2NaOH + 2O_2 + H_2O \rightarrow Na_2TeO_3 + 2Cu(OH)_2} \qquad (81)$$

$$\mathrm{2Cu_2Te(s) + 4NaOH + 3O_2 \rightarrow 2Na_2TeO_3 + 2Cu_2O + 2\,H_2O} \qquad (82)$$

Selenium extraction:	90%
Sulphur extraction:	90%
Arsenic extraction:	75%

2.2.7 High pressure NaOH leach to treat a copper sludge

In a European patent application[4], a process is provided in which the products of a SO_2 reduction step are Se and PtSe in sulphuric acid media. Selenium is dissolved and Tellurium remains in the residue with a hydrometallurgical caustic leach.

Element	*%*	*Element*	*%*	*Element*	*%*
Cu	8–30	***Ag***	7–14	***Bi***	0.2–0.7
Ni	4–10	***Au***	0.1– 0.4	***Sn***	0.1–0.8
Se	7–20	***PGMs***	1–4	***SiO2***	0.4–50
Te	1–5	***Sb***	0.1–0.2	***As***	0.3–2
Pb	2–10				

Table 18: Feed composition of a copper sludge

Process conditions

Temperature	: $200^{o}C$
Oxygen partial Pressure	: 340kN/m2
NaOH concentration	: In excess of Se content – 40g/l
Solids	: 200g/l

Process chemistry

$$2Se(s) + 4NaOH + 3O_2 \rightarrow 2Na_2SeO_4 + 2H_2O \qquad (83)$$

$$2Te(s) + 4NaOH + 3O_2 \rightarrow 2Na_2TeO_4 + 2H_2O \qquad (84)$$

With the caustic pressure leach, the following is the results

Element	*% Extraction*	***Element***	*% Extraction*
Cu	-	***Sn***	89
Ni	-	***Pt***	0.5
Se	99	***Pd***	0.2
Te	0.05	***Rh***	0.002
Pb.	0.4	***Au***	0.02
SiO2	-	***Ru***	0.3
As	95	***Ir***	0.3
Sb	54	***Ag***	0

Table 19: Extractions with a NaOH pressure leach on copper sludge

In a literature study done by Viljoen[25] on the available processes for the removal of impurities from a secondary leach residue, the following was noted:

At Canadian Copper Refiners, slimes are pressure leached in H_2SO_4 at 125°C with oxygen to remove Cu and Te, without leaching Se and Ag. The Te is then removed by contact with metallic copper at 100°C and the precipitate leached with NaOH and air to form sodium telluride, which is then precipitated by a pH adjustment step to pH 5.7

$$2Cu_2Te(s) + 4NaOH + 3O_2 \rightarrow 2Na_2TeO_3 + 2Cu_2O + 2H_2O \qquad (85)$$

Jennings[33] proposed a process for slimes treatment. This involved a pressure leach in dilute H_2SO_4 at 110°C, 345kPa O_2 for 3 hours. The leach liquor at boiling point was treated with Cu shot to precipitate Cu_2Te. The Cu_2Te was leached in dilute H_2SO_4 at 65°C with O_2 to dissolve the Cu, leaving elemental Te that could be purified by vacuum distillation. The residue after the pressure acid leach was pressure leached in NaOH with O_2 in a two stage counter current leach, removing most of the Se as Se (IV).

$$Se(s) + 2NaOH + O_2 \rightarrow Na_2SeO_3 + H_2O \qquad (86)$$

This reaction proceeds at 90°C and 350kPa O_2

$$Ag_2Se(s) + 2NaOH + O_2 \rightarrow Na_2SeO_3 + 2Ag + H_2O \tag{87}$$

This reaction requires 160–180°C and 350kPa O_2.

However, at the higher temperature Se (IV) can be oxidised to Se (VI), leading to difficulty in the oxidation of elemental selenium, therefore a 2-stage counter current leach was implemented to overcome this problem. The Se in solution is recovered in three steps:

(i) Neutralisation to pH 5–6, with removal of precipitated impurities Pb, As and Si.
(ii) Acidification with H_2SO_4
(iii) Gassing of solution with SO_2 at atmospheric pressure to precipitate Se

Unfortunately, in the above survey, no extraction results or feed compositions were noted.

Copper can be recovered from sulphide ores in caustic media with an oxidising gas under pressure (Haskett[34]). The Cu is dissolved as $Cu(OH)_4^-$ and the leach solution can be loaded to up to 10g/l Cu. Fe(II) is oxidised to Fe(III), which hydrolyses to insoluble ferric oxide.

2.2.8 *NaOH leaching performed under pressure conditions with oxygen on a final PGM concentrate*

In a study done by Craig[26], in order to remove sulphur and selenium to acceptable levels in the final PMR feed concentrate, the following process conditions were tested.

Pt %	***Pd %***	***Au %***	***Rh %***	***Ir %***	***Ru %***	***Ag ppm***	***S %***
22.1	12.7	1.2	1.9	0.64	2.6	na	6.1
Se %	***Te ppm***	***Pb ppm***	***Si %***	***Cu %***	***Ni %***	***Fe %***	
5.7	9054	na	11.7	1.7	0.95	2.4	

Table 20: Feed concentrations of a PGM concentrate

Process conditions

Temperature : 150 & 200°C
Oxygen : 1800kPa
NaOH concentration : 0.5, 1, 1.5 & 3N
Reaction time : 5 hrs
Solids: Liquid : 1:4

When a PGM concentrate was exposed to a weak caustic solution (0.5N), under pressure, precious metal dissolution was minimal but still afforded good S extraction (85%) and good Se extraction (56%). When a stronger caustic solution (3M) was used, under the same conditions, extraction increases, ie S (92%) and Se (94%). The use of higher strength caustic solutions (3N), at 150^{o}C and 200^{o}C, resulted in significant leaching of precious metals, particularly Pt and Ru, but the use of carbon dioxide under pressure was effective at selective re-precipitation of the values.

Effective removal of sulphur was dependent on the use of the higher temperature (200°C) and required a minimum of 1N caustic strength. It was found that some other deleterious elements were leached to varying degrees, depending on the conditions. Selenium was readily leached at both temperatures and at all caustic strengths used, except for 0.5 N, where only 56% of the selenium was leached. Removal of arsenic was poor at lower caustic strengths and most effective (>90%) where higher temperatures (200°C) and strong caustic solution (3N) was used. Removal of osmium followed a similar trend to that of arsenic; it appeared more reliant on the higher temperature (200°C) and higher caustic strength (3.0 N) for effective removal (78%).

The results obtained and shown in **Table 21** indicate that both temperature and strength of the caustic solution directly influence the leach behaviour of this final concentrate. The weaker strength of caustic solution, 0.5 N, did not result in measurable precious metal solubilisation, while it provided moderate leaching of sulphur and selenium. Maximum removal of these elements was achieved when 1N caustic was used. During the treatment of caustic pressure leaching at 3N, precious metals were solubilised to varying degrees, but this could be reversed if the leach was followed directly by a carbon dioxide treatment. The results showed that when leach conditions of 200°C and 1.5 N caustic were used, maximum removal of sulphur, selenium and arsenic was achieved; 1N caustic resulted in minimum dissolution of precious metals. The carbon dioxide treatment was shown to be effective for re-precipitation of solubilised precious metals. The effect of the caustic/carbon dioxide process on the remaining precious metals solubility under chlorine/hydrochloric acid and subsequent precious metal speciation was investigated.

Elements leached using various caustic strengths at 200 °C.				
% Leached				
Element	***0.5N Caustic***	***1N Caustic***	***1.5N Caustic***	***3N Caustic***
Pt	$<2.9 \times 10^{-5}$	$<2 \times 10^{-5}$	0.169	1.70
Pd	0.003	$<7 \times 10^{-5}$	$<2 \times 10^{-4}$	0.031
Au	0.001	$<2 \times 10^{-4}$	0.056	0.487
Rh	0.023	0.003	0.001	0.031
Ir	0.002	0.001	1.10	1.43
Ru	0.001	0.001	5.70	35.6
Os	0.409	1.49	56.4	79.6
S	85.4	94.2	92.0	91.7
Se	56.2	93.7	88.3	93.5
As	1.54	47.0	84.7	79.7
SiO_2	n.d.	0.997	37.1	29.7

Table 21: Extraction results after a NaOH leach on a PGM concentrate

Summary of possible NaOH leach processes

General pressure conditions using oxygen and high temperatures

1 Sulphur and selenium extraction is virtually complete in sulphide ores.

2 Tellurium does not extract because it is converted to the hexavalent form, which is not soluble.

3 Selenium is soluble in the hexavalent form, but difficult to recover.

4 Silica extraction varies between 20 – 30%

5 Base metals (Cu, Ni, Fe) extract at lower NaOH concentrations to between 40 – 70%, due to the formation of oxyanions.

6 PGM dissolution under oxygen pressure conditions is very limited.

7 Pb dissolution also seems very limited as it is converted to Pb(IV).

General atmospheric conditions using oxygen and temperatures of 80°C

1 Oxygen usage under very slight pressure conditions on a selenium and tellurium residue had 90% Se extraction, but tellurium extractions were only 2 %.

2 Tellurium extractions increases when the leach is conducted for only 20 minutes, as tellurium is then converted to the tellurite form, which is soluble. Extraction data however could not be obtained.

3 Sulphur extraction under these conditions was above 90%.

4 Platinum extracted to 35% at $80^{o}C$, but only 0.2% at $50^{o}C$.

General atmospheric conditions without any oxygen addition and temperatures of $80^{o}C$

1 PGM extraction was very limited.

2 Elemental sulphur extraction is complete. It is however not clear how much sulphide sulphur extracted.

3 Silica extraction was higher than 80%.

4 Lead extraction in an oxide ore was higher than 80%. Lead in NaOH media is soluble if exists in the Pb(II) form, but when oxidised to the Pb(IV) form it precipitates.

5 Copper, Nickel and iron is not soluble, and is present as hydroxides.

SECTION 3

OBJECTIVES AND SCOPE OF PRESENT INVESTIGATION

The continuous copper pressure leach test (CPL) work which was done for the new BMR process had two distinct periods. During **Period A,** a highly oxidative leach was done with the aim of extracting as much copper, nickel and sulphur from the residue as possible without the addition of extra Fe as an oxidant to the leach, and with the secondary aim of keeping the selenium, tellurium and PGM extraction as low as possible. As the leach did not yield sufficient extraction for copper and nickel, it was decided to add Fe to the CPL leach **(Period B)**, to see if extraction of these metals would improve. The subsequent test work then largely succeeded in achieving these objectives.

The compositions of the residues produced during these two periods are shown in **Table 22**. Evaluating these and the mineralogical data in Table 26, it is clear that with a residual Cu grade of 37–53% remaining in the residue after the continuous leach, an additional leach had to be employed to further upgrade this residue.

The amount of residue which was available from the CPL test work for the present study was unfortunately very small. As not enough residue during the B Period was produced, a decision was taken to use Period A residue for any further test-work, and then to compare the results against those from a few leaches with the small amount of residue returned from Period B.

Scoping tests were then performed, firstly with a primary leach residue from the current operation in order to check how well the conditions selected would perform. However, this residue produced a lot of agglomeration that assembled at the bottom of the autoclave and did not take part in any further leaching. This agglomerated material was then analysed and its sulphur content was found to be 63%, which is very similar to the residue produced during Period B. This then led to the conclusion that the residue which is likely to be produced in the new BMR process should not be treated any further with a sulphuric acid leach, unless the elemental S portion can be reduced or eliminated.

The search for a process in order to leach this residue then started, and it was found during the literature survey that an atmospheric NaOH leach would be suitable to dissolve the elemental S in this residue. In performing an atmospheric NaOH leach, however, the effects on the remainder of the elements then needed to be tested under various conditions, as well as the extraction of elemental S that could be achieved with this type of leach. Although not enough CPL residue was available, sufficient of this agglomerated residue was produced from the primary leach residue (PLR) to both test an oxidative NaOH leach under various conditions and find the optimum manner to get this elemental S leached and the residue cleaned, so that further processing via a sulphuric acid leach could be done.

The test work described here started with NaOH batch leach tests, using the PLR residue, to determine the optimum conditions under which the CPL residue can be processed so that it contains as little elemental S as possible. From literature, it was clear that good extraction of elemental S could be achieved in a NaOH medium even without any oxygen addition, and this could be achieved either atmospherically or under pressure[11]. It was decided to test an oxidative NaOH leach in order to use this opportunity to extract as much of the Se and Te as possible in this step, and to observe the influence this would have on Cu, Ni and PGM extraction. The literature indicated that under pressure conditions, good Se extraction could be achieved, but very little Te extraction. This would then act as a possible separation step between these two elements. Under atmospheric conditions, Pt would possibly dissolve at low NaOH concentrations whereas Cu and Ni would possibly dissolve under pressure conditions. Other literature[22] indicated, however, that Cu and Ni would not leach under atmospheric conditions but a much higher NaOH strength was used in this instance. It was therefore decided to test this residue using an atmospheric, oxidative caustic leach in a 2M NaOH strength solution. If this could be successful, then a sulphuric acid leach could be employed to extract as much of the Cu and Ni as possible.

The principal objective of this study is to produce a PGM rich residue that is acceptable for processing in the PMR thereby avoiding the current toll refining route altogether. After gathering information during the literature survey and given the chemical composition of the final residue to be produced, it was decided to investigate optimal conditions for a caustic oxidative leach for S and Se removal from the residue under consideration, using the PLR agglomeration as a residue. If successful, and the optimum conditions were determined, this would then be used to prepare sufficient of the A residue via a NaOH continuous leach, so that further test work employing an acid oxidative pressure leach can be done. The optimal conditions would then be investigated for maximum extraction of Cu, Ni, Fe and other minor elements like Se and Te. The results from this work would then be used to develop a preliminary process flowsheet for the treatment of this residue.

	Res A	**Res B**	**PLR Feed (%)**	**Agglomerated Material from leach**
Element	***Assay (g/t & %)***	***Assay (g/t & %)***	***Assay (g/t & %)***	***Assay (g/t & %)***
Cu %	53.29	37.75	48.5	11.3
Ni %	1.57	1.5	12.9	12.7
Fe %	0.1	1.76	3.7	8.5
Co %	580	320	NA	NA
S %	37.1	57.25	27.2	62.6
S^0	9.3	36.4	NA	NA
Pt	45.2	105	NA	NA
Pd	819	2150	NA	NA
Rh	42.2	78	NA	NA
Au	108	287	NA	NA
Ru	47	128	NA	NA
Ir	14.9	35.4	NA	NA
Se	1610	1793	NA	1595
Te	170	302	NA	144
Pb	118	333	NA	48
As	115	132	NA	104
Sn	58.3	56	NA	NA
Mn	<0.02%	<0.02	NA	NA
Bi	6.56	14.7	NA	NA
Sb	55.5	89.5	NA	NA
SiO_2	NA	NA	NA	0.46

Table 22: Composition of different residues

The literature survey on the oxidative sulphuric acid pressure leach indicated that variations in leaching conditions could have a huge impact on the type of residue being formed. The objectives to achieve is the following:

(i) Leach as much of the base metals as possible.

(ii) Keep the Fe in solution when leach, without reprecipitating,

(iii) Leach as little of the PGM's as possible

(iv) Remove as much of Se and Te as possible.

The decision were made to do various tests in order to get the best leaching conditions possible, which would be achieved by varying conditions of oxygen partial pressure, temperature, influence of extra ferrous addition, varying the acid conditions, and varying the agitation rates.

SECTION 4

CAUSTIC BATCH LEACH

4.1 Introduction and Objectives

The main purpose for investigating a caustic leach as a possible treatment route for copper pressure leach residue (CPL), is as follows:

(i) Pre-treatment of the CPL residue for the removal of elemental sulphur and finding the optimum conditions – it is believed that sulphur prevents the extraction of the major base metal elements, copper and nickel due to sulphur ball formation.

(ii) Determining the impact of the different leach conditions on the major base metals (Cu/Ni/Fe), amphoterics and other trace elements.

The caustic pressure leach process leaches sulphur compounds, selenium, arsenic and silica to various extents, depending on conditions. (See summary of Section 2 on NaOH processes) This could be used to separate most of the above elements from the PGMs, because the indications are that this leach, if performed under certain conditions, will keep PGM dissolution to a minimum as shown in the literature review. Although this leach will separate some of the elements present in the copper pressure leach residue, it is unlikely to attack any of the Pb, Ag or Te according to literature. These elements are problematic in the current PGM refinery process and must be removed.

4.2 Experimental Matrix

A test matrix (eight tests) was designed based on three variables, ie time, temperature and initial solids loading, as indicated in **Table 23.**

Test number	*Time (min)*	*Temperature (°C)*	*Solids loading (g/l)*	*g NaOH/ g residue*
1	60	50	100	0.8
2	60	80	50	1.6
3	20	80	50	1.6
4	40	80	50	1.6
5	30	80	50	1.6
6	30	25	50	1.6
7	30	50	50	1.6
8	60	80	200	0.4

Table 23: Test matrix for NaOH batch leach

These eight tests were conducted and, for each element, graphs of extraction vs. time, temperature and solids loading were plotted. The optimum conditions can be selected from these graphs. From the literature[24], solids loading has a marked impact on extraction. The loading recommended in the literature is above a ratio of 1.07g NaOH / g residue. Most tests were performed at 1.6g NaOH/ g residue.

4.3 Experimental

4.3.1 Feed materials

Solids (PLR sulphuric acid pressure leach sulphur agglomeration)

A sulphuric acid pressure leach was conducted as for the scoping tests, because the residue from the CPL leach was not enough to use for scoping tests as well, as described in detail in the proposal section. This PLR leach was performed under the following conditions:

Temp : 140°C
pO_2 : 340kPa
Solids loading : 100g/l
Acid concentration : 60g/l
Ferrous concentration : 2g/l
Agitation rate : 280rpm

Element	***PLR Feed (%)***	***Agglomerated Material from leach (%)***
Cu	48.5	11.3
Ni	12.9	12.7
Fe	3.7	8.5
S	27.2	62.6
Se	NA	1595
Te	NA	144
Pb	NA	48
As	NA	104
SiO_2	NA	0.46

Table 24: Composition of PLR feed material and agglomerated product

The scoping tests produced a substantial amount of agglomeration that did not leach, and on closer examination, this was ascribed to the high proportion of elemental sulphur being present in the residue. (Refer to **Table 24** for compositions.)

4.3.2 Experimental procedure

The eight tests were performed in a beaker in 2M caustic solution, with the addition of oxygen. The leach time, temperature and solids loading were varied according to the test matrix as indicated in **Table 23**. On completion of the leach, the slurry was filtered through a 10 micron Millipore filter and the residue washed properly with demin water until clean from entrained solution. The volume of demin water added for wash water was measured. The solids were dried at 60^{o}C and the dry mass measured and both solution and solids were sent for analysis. The solids were analysed for Ni, Cu, Fe, S, Si, Se, Te, Pb and As and the solution samples were analysed for Na_2SO_4, Ni, Cu, Fe, Se, Te, Pb and As.

4.3.3 Analytical procedures

In the solution samples, concentrations of copper, iron and nickel were determined by AA spectroscopy. Concentrations of lead, selenium, tellurium and arsenic, were determined by inductively coupled plasma spectrometry (ICPS). The sulphate content of solutions was determined by precipitation with BaCl and subsequent ICP analysis. Selected solution samples were also analysed for PGM contents by ICPS. Solids samples were dissolved in aqua regia and analysed for copper, iron and nickel, lead, arsenic, selenium and tellurium content by ICPS and the concentrations of sulphur (sulphide and elemental) were determined by the LECO analyser.

4.3.4 Calculations

Solids extraction calculations are based on differences between total initial element mass in feed and final element mass in residue. Similar calculations were done to determine solution extractions. The calculation of sulphide sulphur and elemental S could be erroneous because the base metals in solids could be in hydroxide form and not in sulphide form. In the extraction calculations, an assumption was made that all the base metals were in the sulphide form after washing. The total sulphur content was determined with the LECO analyser and the base metals in the solids were then determined and assumed to be all present in a monosulphide form, and the total sulphide sulphur were then calculated from this. This was subtracted from the total sulphur and the total elemental sulphur was then determined. Sulphur and silica extraction calculations were based on solid assay results, while the rest were based on solution assay results. Accountabilities were calculated and expressed as the sum of the total element in solids and solution, as a percentage of total elements in initial solids. All assay results and accountabilities are shown in Appendix 1.

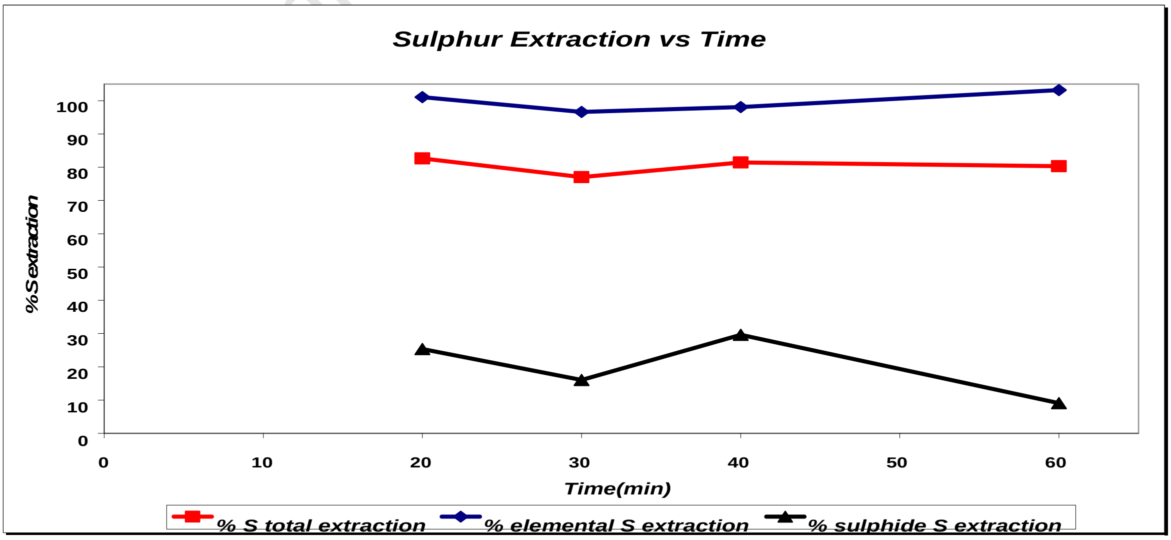
4.4 Results and Discussion

Results are presented by discussing extractions of each element in terms of varying time, temperature and solids concentration, in the following order: sulphur, selenium, tellurium, lead, base metals (Cu, Ni, Fe), and silica. These are all the elements that will have an impact on the PMR and which need to be removed from the refinery's circuit to prevent high recirculation loads.

4.4.1 Sulphur extraction

Sulphur extraction with time

The temperature (80°C), solids loading (50g/l) and NaOH concentration (2M) have been kept constant, while the time period for the leach was varied. Times used were 20, 30, 40 and 60 minutes.

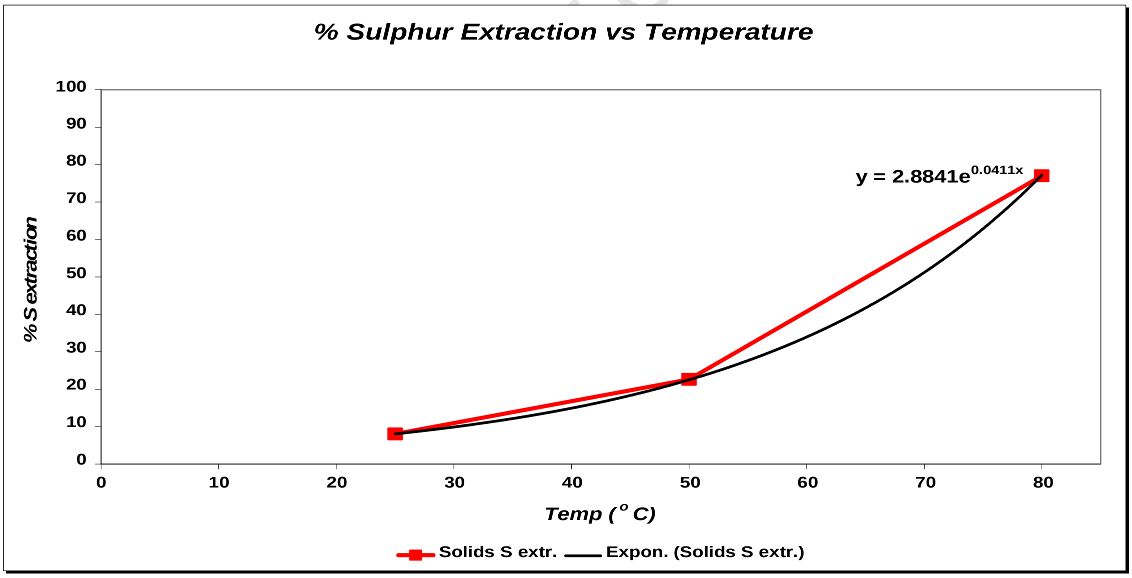


Graph 1: NaOH Bx leach – sulphur extraction vs. time, using solids assays for calc.

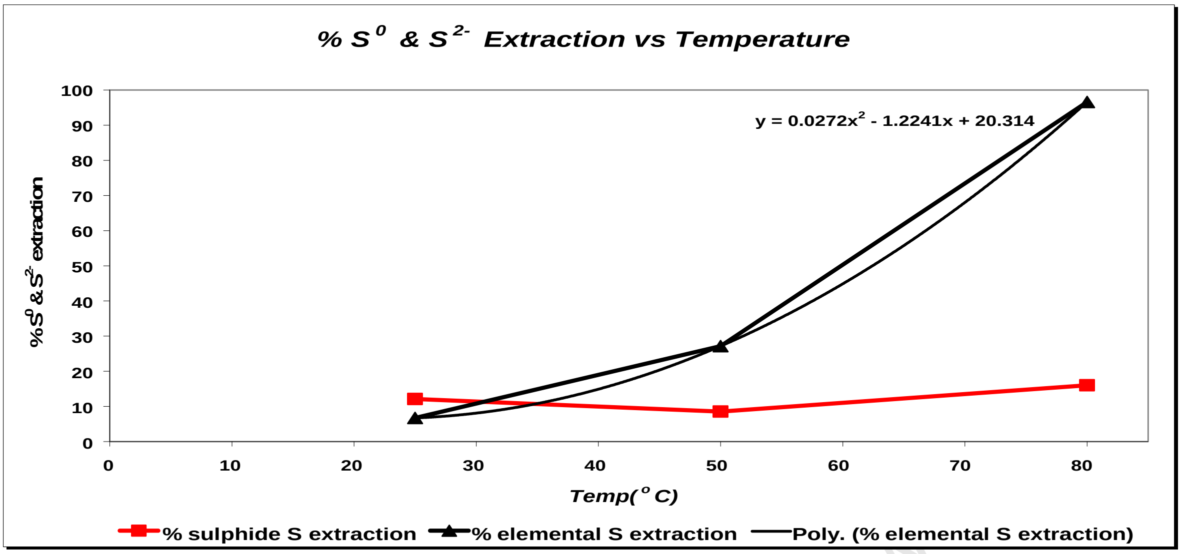
It appears that sulphur extraction shows no particular correlation to time (**Graph 1**), and after 20 minutes most of the sulphur is already extracted. It also appears as if all the elemental sulphur in this residue was dissolved, and if calculating from the BM analysis, the sulphide sulphur has also been extracted between 20–30%. This, however, is based on an assumption that all of the base metals in the final residue are associated with sulphur, as CuS, NiS, FeS. However, this is not the case, as can be seen from the mineralogical analysis in Table 26 done on the actual CPL residue following the NaOH leach. This analysis shows that some of the base metals have been converted to oxides and hydroxy-sulphates.

Sulphur extraction with temperature

The time (30 min), solids loading (50g/l) and NaOH concentration (2M) have been kept constant, while the temperature period for the leach was varied. Temperature variations were 25, 50 and 80°C.



Graph 2: Sulphur extraction vs. temperature, using solids assays for calc.

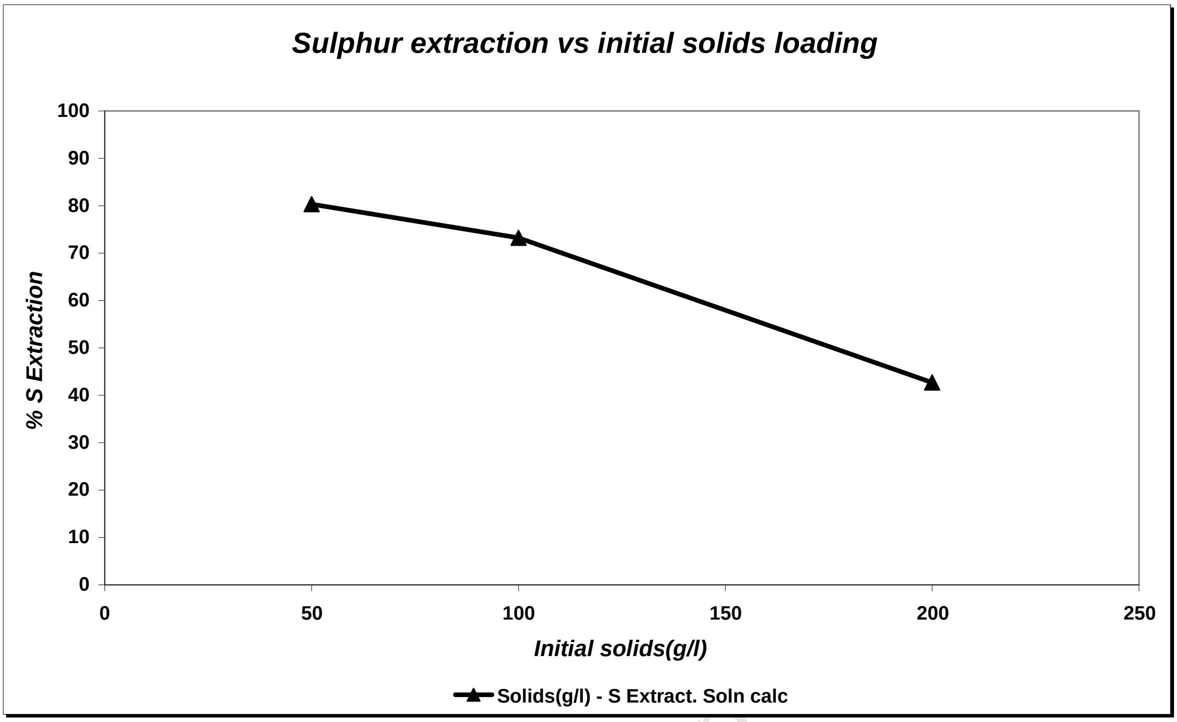


Graph 3: Calculated elemental and sulphide sulphur extractions vs. temperature, using solids assays for calculation

There is a strong correlation between sulphur extraction and temperature, with 80^{o}C being the best of the three values tested. The sulphide sulphur extractions varied between 10–20%, which shows no correlation to temperature. However, the elemental sulphur extraction shows a strong correlation to temperature at 80^{o}C and it had all been dissolved, within 30 minutes, confirming the above observations on time.

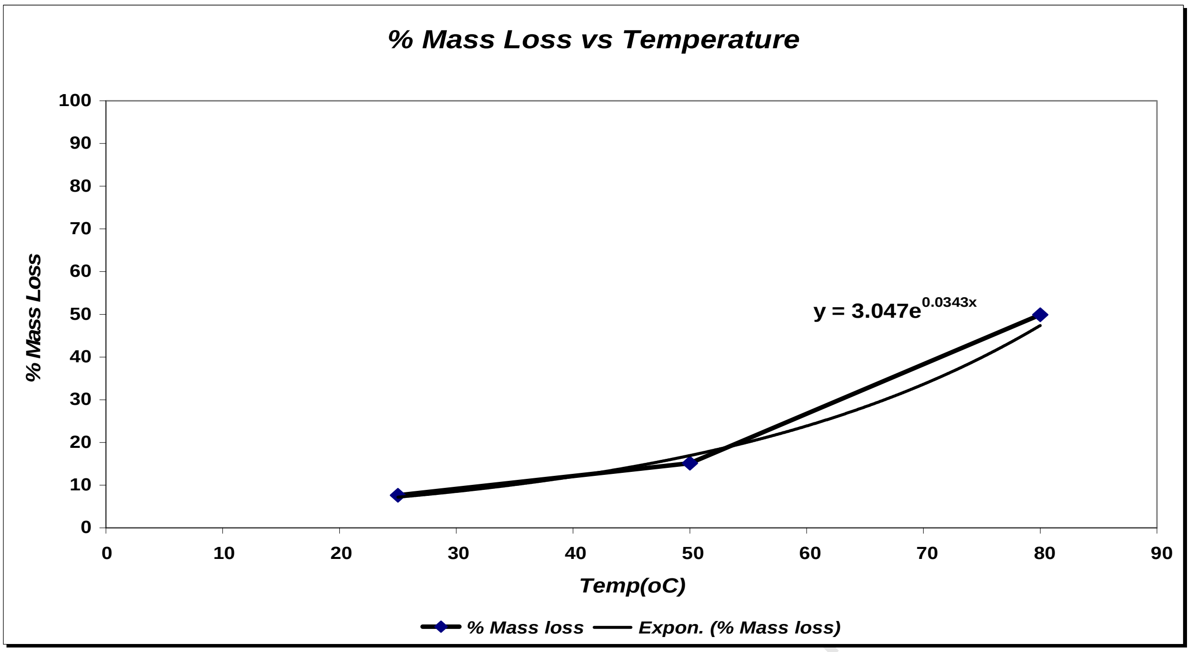
Sulphur extraction with initial solids concentration

The time (30 min), temperature (80^{o}C), and NaOH concentration (2M) were kept constant, while the solids loading for the leach was varied. Solids loading variations were 50, 100 and 200g/L



Graph 4: Sulphur extraction vs. solids loading, using solids assays for calculation

It appears as if there is a definite correlation between solids loading and sulphur extraction, which indicates the lower the solids loading, the better the sulphur extraction. In the higher solids loading test, the lower sulphur was due to extremely high solids loading. At higher solids loading, more and more NaOH is neutralised, resulting in a shift in pH. Also, the higher solids loading affects the gas-liquid mixing and the oxygen mass transfer rate into the slurry. It is postulated that the system became mass transfer limited at the higher solids loading. The test with the highest solids loading was done at a gNaOH: g solids ratio of 0.4, while the optimum ratio was found to be 1.07 from the literature[24].



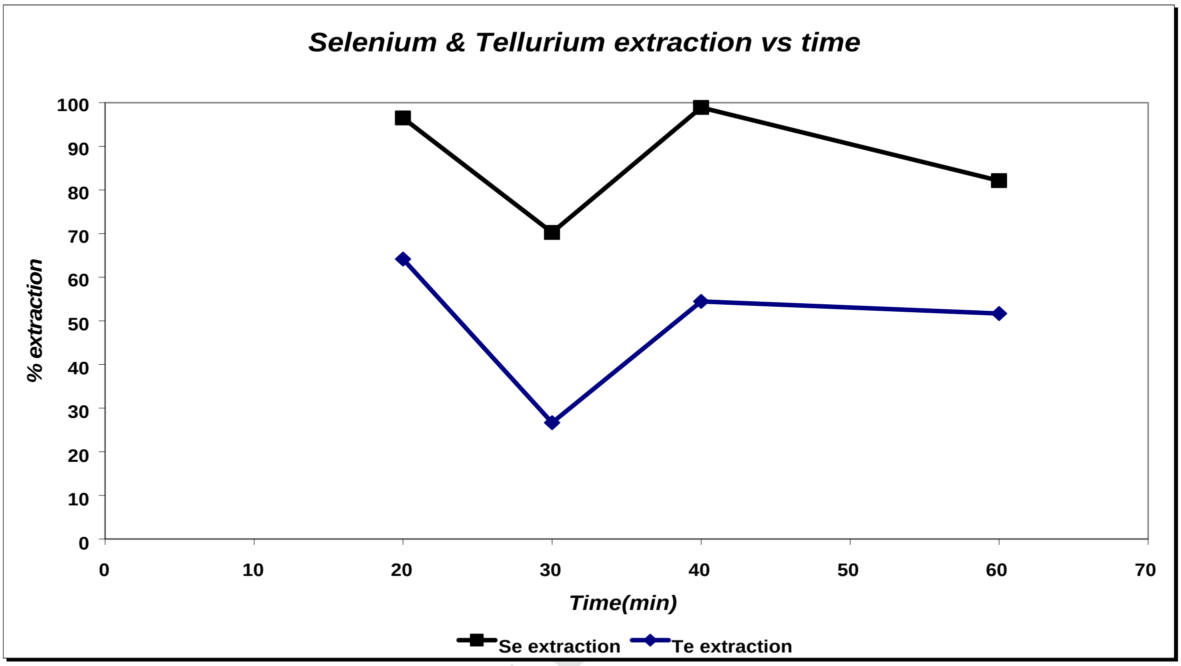
Graph 5: Percentage mass loss vs. temperature

The graph indicates that the percentage mass loss from the solids mainly follows the sulphur extraction, as sulphur is the main element present in the PLR solids (sulphur agglomeration portion). It also indicates a similar trend that temperature is the main driving force for elemental sulphur dissolution. The average S extraction was calculated to be 80%. If this amount of S was extracted, it would calculate an approximate 50% mass loss in the tests done at 80^{o}C. The major base metal sulphide mass and hydroxide mass does not differ very much, therefore this difference is unlikely to have a large impact on the percentage mass loss. The percentage mass loss and percentage S extraction then compares extremely well, indicating that the sulphur extraction data is very reliable.

4.4.2 Selenium and tellurium extraction

Selenium and tellurium extraction with time

The same conditions were used as indicated with sulphur extraction vs. time

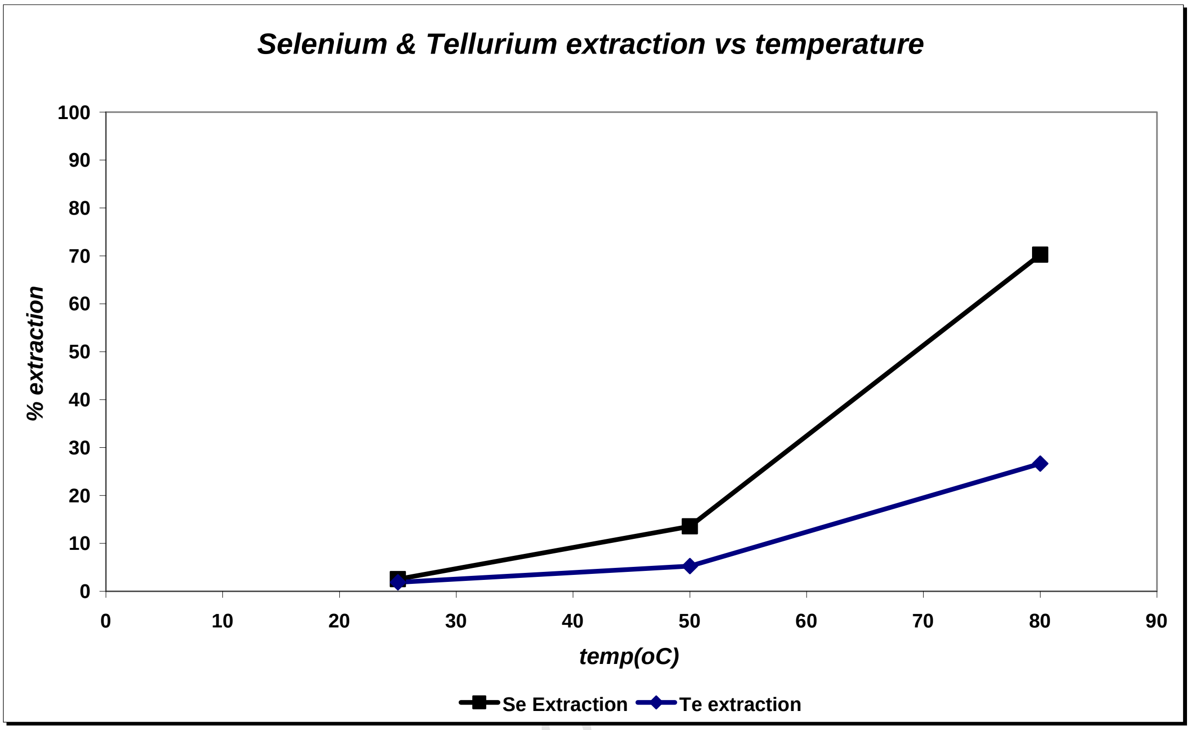


Graph 6: Se & Te extraction vs. time, using soln. assays for calculation

It appears as if selenium dissolution is between 70–100% and tellurium dissolution between 25–60% at 80°C and 50g/l solids loading (Graph 6). Neither element really shows that this is residence time related, and as with sulphur extraction, it happens within the first 20 minutes. The dip at 30 minutes appearing in both elements could be analytical error, but this shows when using either solids assays or solution assays for extraction calculations. However, according to literature[19], tellurium should precipitate as a sodium tellurate if left to leach for longer than 20 minutes. If this was the case, the selenium in turn, if present as the selenite or selenate species, would remain soluble. Therefore, selenium in **Graph 6** should not show a dip as well. Unfortunately, the speciation of neither selenium nor tellurium was determined in the present case.

Selenium and tellurium extraction with temperature

The same conditions were used as indicated with sulphur extraction vs. time

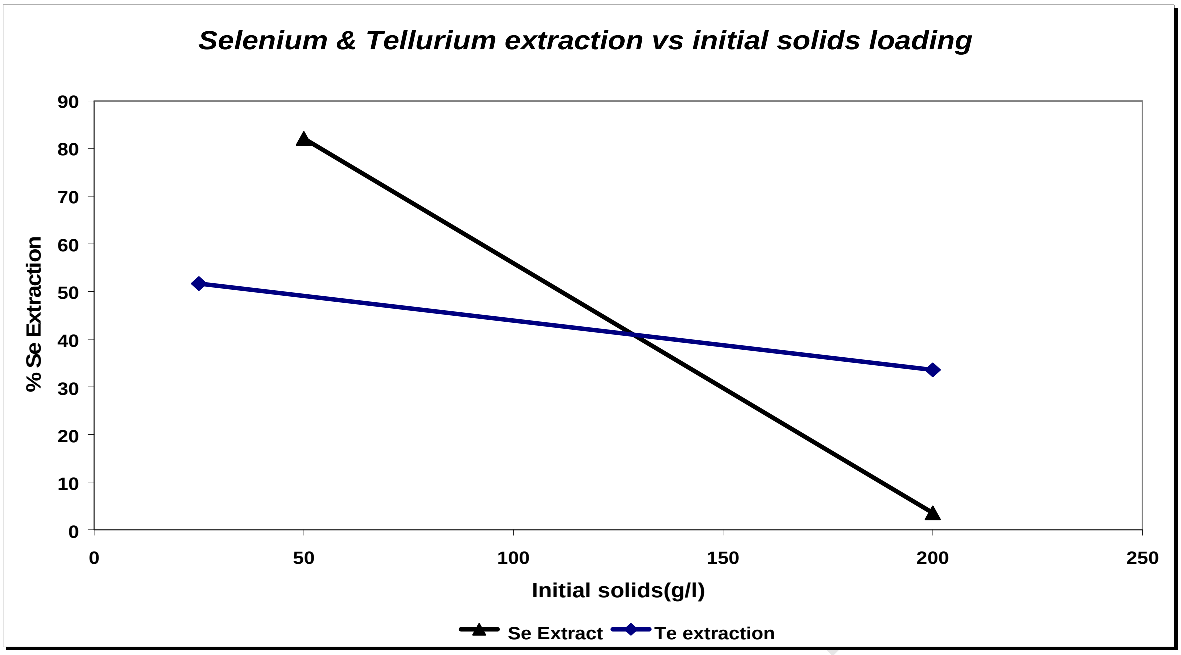


Graph 7: Se and Te extraction vs. temperature, using solution assays for calc.

Selenium and tellurium extraction in 2M caustic solution is highly temperature dependant **(Graph 7)**. The test performed at 80^{o}C, is the same test performed at 30 minute testing for time dependency **(see Graph 6)**. This test gave lower results for both selenium and tellurium, and, if assuming that there was an analytical error on this test, then much higher selenium and tellurium extractions can be achieved. Both selenium and tellurium accountabilities appear to be surprisingly good, for the low concentrations measured.

Selenium and tellurium extraction with initial solids concentration

Solids loading does appear to have a significant impact on the extraction of both these elements, ie the higher the solids loading, the lower the extraction.



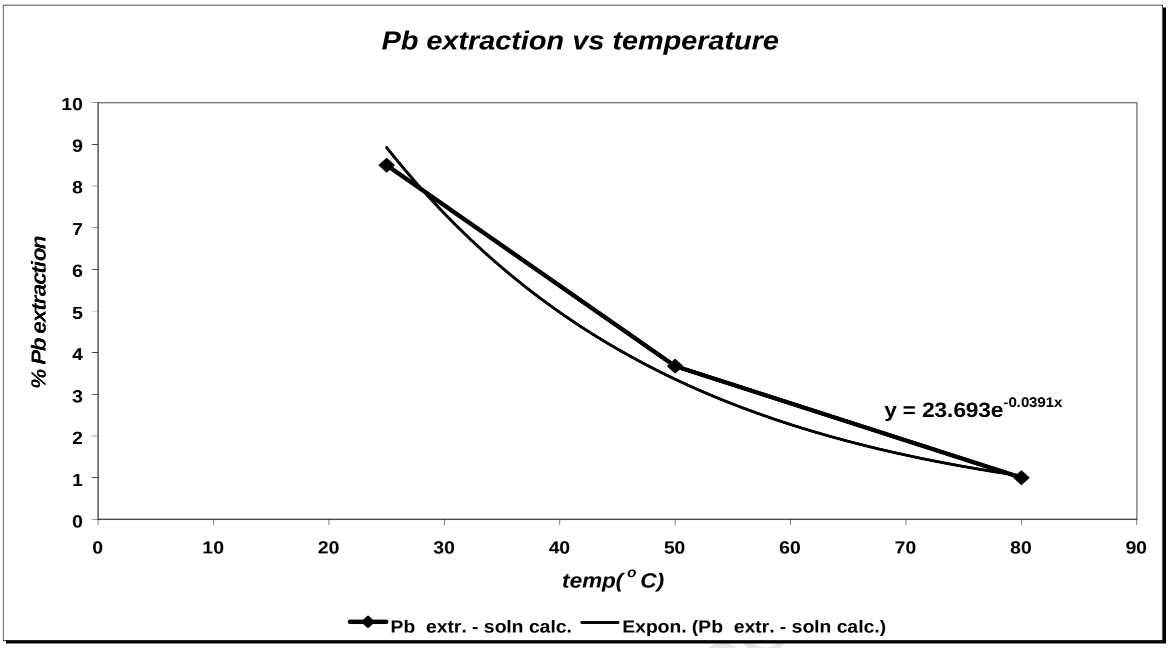
Graph 8: Se and Te extraction vs. solids loading

4.4.3 Lead extraction

Testing if lead extraction has any correlation to time

The conditions were the same as those indicated for sulphur extraction vs. time. It appears as if lead dissolution is not time-related at 80°C and 50g/l solids loading if calculated from solution assays. In fact, the maximum lead extraction under the above conditions is 1%.

Lead extraction with temperature



Graph 9: Pb extraction vs. temperature, using soln. assays for calc.

It does appear as if lead extraction in 2M caustic solution is temperature dependant, if looking at solution assays. But, extractions are still very low, even at 25°C, and drawing any conclusions from the very low assay results is too risky. This is, however, worth investigating further.

Orhan[2] indicated that lead extraction is 90% at 95°C, high NaOH concentration (10M) with no oxygen input from an oxide form. Stoll [24], also found that Pb (II) is soluble, and 76% extraction could be achieved with 2M NaOH at 90°C and no oxygen input. He states, however, that if Pb is oxidised to Pb (IV), it is insoluble and it precipitates. This process provides an opportunity to remove lead, based on the differential solubility of the oxyanions of lead. When lead is in the Pb (II) form, it exists as $HPbO_2^-$ ion in concentrated caustic solution, but if oxidised to Pb (IV) form, its solubility is significantly reduced.

$$Pb(OH)_2(s) + OH^- \rightarrow HPbO_2^- + H_2O \qquad (88)$$

$$Pb_3(AsO_4)_2(s) + 9OH^- \rightarrow 3HPbO_2^- + 2AsO_4^{3-} + 3H_2O \qquad (89)$$

The results achieved in the literature stated above were, however, done without oxygen addition. The results achieved by the tests performed during this test work, do not show much lead extraction under any of the conditions tested. In fact, if lead did solubilise, then it was in the lower temperature range. A possible explanation could be that the oxygen oxidised the Pb to Pb (IV), which then precipitated again. The oxidation at the higher temperatures might be more rapid, therefore resulting in a lower overall solubility as the temperature increases.

4.4.4 Base metals

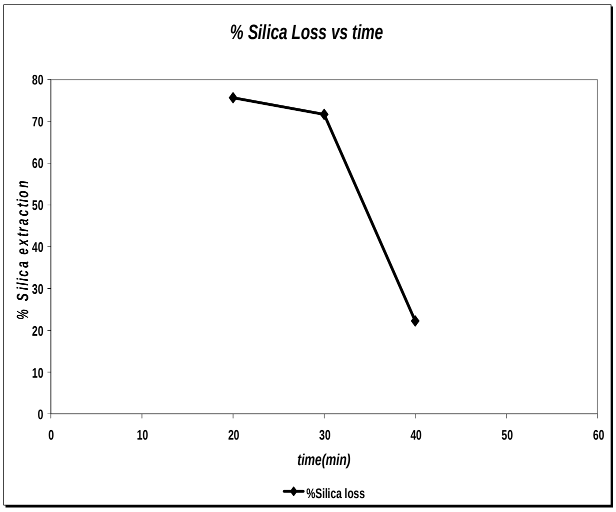
It appears from extraction calculations from solution assays that no nickel and iron dissolution occurred. Copper showed some dissolution, ie 1–2% extraction, which showed in a bluish colour in the solution. This colour did not show in all of the tests, and the test where it was observed, had 80 and 110 ppm Cu dissolved. Literature[34] showed that Cu is dissolved as $Cu(OH)_4^-$ and the leach solution can be loaded to up to 10g/l Cu under oxidising conditions with higher NaOH concentrations. The results were consistent with test work performed by Stoll [24], which states that Cu will precipitate as a hydroxide. In work done by Orhan[2], there was Cu dissolution at much higher NaOH concentrations. However, neither of these test work campaigns used oxygen.

4.4.5 Silica

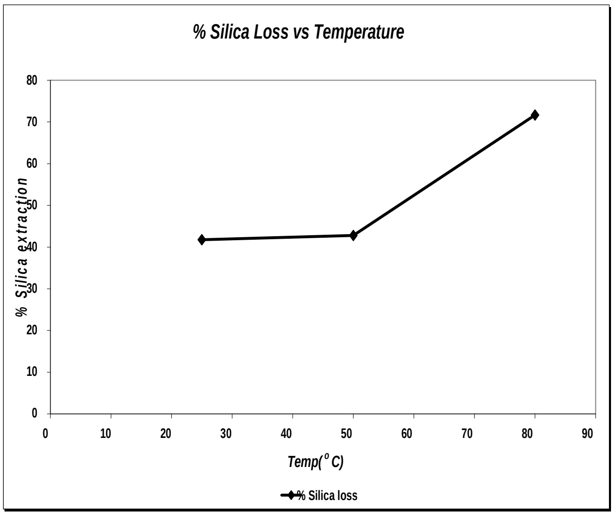
The test conditions were similar to those as indicated with sulphur extraction vs. time and temperature. It appears as if dissolution is between 70–80% up to 30 minutes leaching time **(Graph 10)**. The sudden drop in silica dissolution at 40 minutes is strange. Rivett, Mracek and Robinson[10] showed that silica extraction in excess of 90% can be achieved under much the same leaching conditions with 1.25M NaOH solution, except that no oxygen was used during those tests. Dunn[11] only achieved 20% silica dissolution at a much lower NaOH concentration (0.25M) and much higher temperature (200°C) using oxygen. Craig (2004)[26] achieved a much better extraction (37%) using a high temperature, high oxygen partial pressure leach. It appears as if the dissolution of this element could be both temperature and time related, but more tests need to be done in order to confirm. The NaOH strength definitely has an impact on extraction of this element. Also, if using oxygen, this would alter the species being leached, which possibly has different solubilities.

$$2SiO_2 + 4NaOH + O_2 \rightarrow 2Na_2SiO_4 + 2H_2O \qquad (90)$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \qquad (91)$$



Graph 10: Silica extraction vs. time



Graph 11: Silica extraction vs. temperature

4.5 Conclusions

The analytical data shows that the 2M caustic solution is effective in removing all the elemental sulphur. Elemental sulphur extraction is strongly temperature dependant, with sulphide sulphur not really showing the same tendency, although still between 10–20% sulphide sulphur is extracted within a very short space of time (20 minutes) at 80°C. However, this is dependant on temperature and initial solids loading, and from the different conditions tested, it shows that at a temperature of 80°C and a solids loading of 50g/l the best results are achieved. Time does not show to be a factor for consideration as far as sulphur extraction is concerned, but a higher solids loading appears to have a negative impact on both elemental and sulphide sulphur extraction.

It does not appear if any of the base metal sulphides (Cu/Ni/Fe) are dissolving. However, again large discrepancies between calculated solution and solids extractions have been found. It is assumed that from the above sulphide sulphur extractions that these BMs are dissolved in the same ratio as the sulphide sulphur dissolution, but re-precipitate as some metal hydroxide or oxide species immediately.

Copper accountabilities are fairly good, and the copper concentrations in solution are on average very low. There were two samples which showed a bluish colour, assumed to be copper. The reason for the slightly higher copper (80 and 110mg/l) is not completely clear and it must be related to either/or residence time/ temperature, but this could not be established as the other tests do not show the same colour. It seems that not all the copper oxidised re-precipitated as a hydroxide/oxide. All other tests resulted in a yellowish to brown colour after leaching with caustic. This could be potentially pH related, but unfortunately the pH was not measured when these tests were performed. Further, it should be noted that copper extraction calculated from solution showed substantially lower values than copper extraction calculated from solids concentrations.

Nickel shows very little extraction and its accountabilities are good. Fe also shows very little extraction. There appears to be between 40–80% dissolution of silica and too few tests with too low assay results to really draw a firm conclusion about this. The literature suggests that SiO_2 should dissolve as indicated in the discussion section.

Selenium extraction is highly temperature dependant and at $80^{o}C$, all selenium is extracted in a 2M caustic solution at 50g/l initial solids loading. It is also shown as with elemental sulphur that selenium extraction happens within the first 20 minutes.

Tellurium extraction is also temperature dependant, and at $80^{o}C$, 25 % tellurium is extracted in a 2M caustic solution at 50g/l initial solids loading after 30 minutes. The higher the temperature in the range tested, the higher the Te extraction. However, it is also shown, as with elemental sulphur, that tellurium extraction happens within the first 20 minutes when tested at $80^{o}C$. The significance of this is that Te extraction after 20 minutes was 64%. This could indicate that Te reprecipitates as a tellurate species if leached any longer than 20 minutes, which is also shown in work done by Steenekamp & Dunn (1999).[26] Hoffmann[1] also indicates that Te in strong alkaline media will be present as a tellurate, and it is used as a separation technique between selenium and tellurium. This can definitely be used in a process flow design for treating the CPL residue to be treated because the tellurite species would be soluble in strongly alkaline media, while the tellurate species precipitates.

Lead did not dissolve under the oxidative conditions employed, nor was it expected to. The literature shows that lead dissolution under these conditions would improve substantially if a non-oxidative caustic leach was employed. This is significant, because Pb extraction would be very beneficial for proposing a process flow.

Arsenic extraction is temperature dependant and at $80^{o}C$ most arsenic is extracted in a 2M caustic solution at 50g/l initial solids loading. It is also shown, as with elemental sulphur, that arsenic extraction happens within the first 20 minutes.

Thus, it can be said that elemental sulphur can be removed from the residue under consideration successfully using an oxidative leach in 2M caustic solution. There is no real benefit in leaching this residue for longer than 20 minutes, as most of the elements that can leach will do so within this time. The temperature of 80°C is however crucial for the extraction of elemental sulphur. There is a benefit in doing this leach at the higher temperatures because, as shown, selenium, tellurium and arsenic extractions are highly temperature dependant. The extraction of these metals would be beneficial, if this material needs to be treated further downstream, after the sulphuric acid pressure leaching of the residue is completed.

SECTION 5

CAUSTIC CONTINUOUS LEACH

5.1 Introduction and Objectives

It has been established via the batch leach tests on caustic that elemental sulphur can be removed to a large extent. The main purpose of the caustic continuous leach is to treat the bulk CPL residue in order to remove elemental sulphur, to find the optimum conditions under which the sulphuric acid polishing pressure leach can be done and to separate as many of the unwanted elements from the CPL residue.

While the main purpose of the continuous caustic leach is the removal of elemental sulphur, it would be interesting, as well as beneficial for proposing a process, to see if the results achieved with the batch leach can be reproduced on a continuous scale.

Therefore, the objectives for the continuous caustic leach test work phase are as follows:

(a) The main objective is to test if the CPL residue can be treated on a continuous basis, to extract as much of the elemental sulphur as possible.

(b) The second objective is to test the behaviour of copper, nickel, iron, tellurium, selenium, lead, arsenic, silica and all the PGMs under fixed conditions as determined during the batch leach test work.

Conditions

Temperature : 80^oC

Time : 60 minutes

Initial Solids loading : 50 g/l

NaOH strength : 2M

g NaOH/ g residue : 1.6 (optimum > 1.07)

Although the continuous leach is set up for a residence time of 60 minutes, only 20 minutes is needed according to the results of the batch leach tests. This is done in order to see what effect the longer residence time would have on a continuous scale, and the possible benefits (or drawbacks) of extending this in the leaching of copper and nickel and trace metals.

5.2 Materials and Methods

5.2.1 *Feed Materials*

- Solids (CPL residue) See **Table 1** and **Table 22** residue A
- See mineralogy of A residue in **Table 26**
- Caustic solution 2M – 80g/l
- Oxygen
- Demin water

NaOH, demineralised water and solids requirements for leach		
Make up 4000ml of 2M NaOH	320	g NaOH
Volume of NaOH @ density 1.51	212	ml NaOH
But, NaOH @ 50%	424	ml NaOH
Make up to 4000ml with demin water	4000	ml
Add solids @ 50g/l	200	g
Time for 4000ml to last	6.7	min
Make up	15	beakers
Total NaOH needed	6	Ltr.
Demin water needed	54	Ltr.

Table 25: Calculations of requirements for NaOH continuous leach

5.2.2 *Equipment*

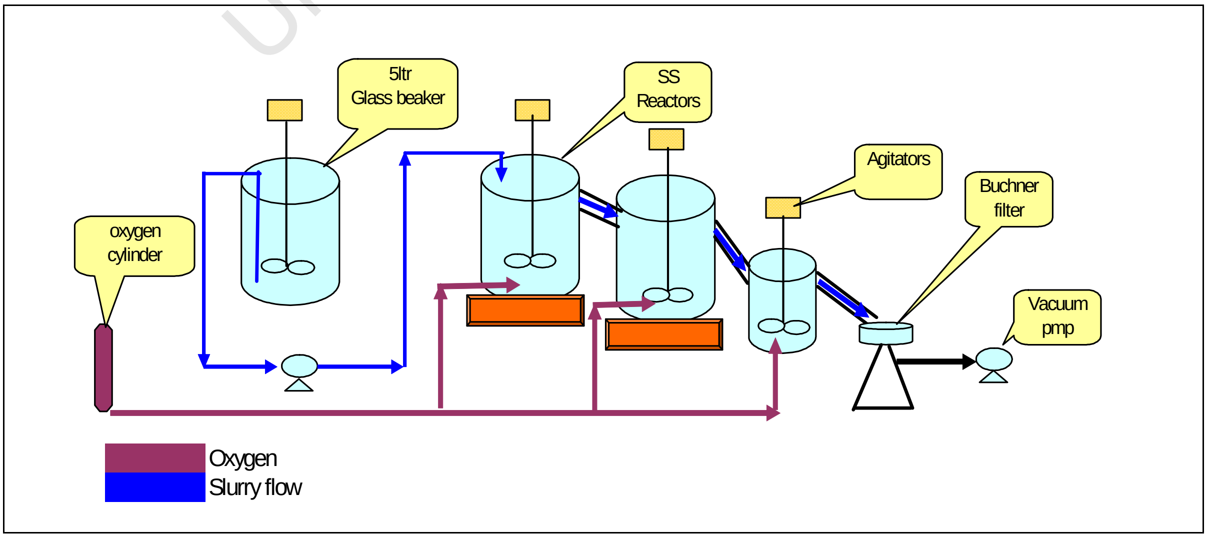


Figure 6: Figure of experimental set up for continuous NaOH leach

3 reactors, fitted with air spargers, still wells

Dimensions	:	2 x 16ltr + 1 x 4ltr
Total volume	:	36 litre.
Diameter	:	250mm
Height	:	360mm
Residence times	:	Reactor 1 & 2 = 27minutes, Reactor 3 = 7 minutes
Agitators	:	Labotec with variable speed 4 x
Rushton type Impeller	:	Sizing

Diameter	83 mm
Height from bottom	83 mm
Impeller blade width	17 mm

A 5 litre glass beaker was filled with 2 M NaOH solution. Solids are added (200g) while agitating the solution, which is then pumped with variable speed into reactor 1 – the reactors are overflowing into one another. Oxygen is added via a sparge tube beneath the impellers. The reactors were placed on top of hotplates and the temperature controlled at 80°C. The overflow slurry from reactor 3 is filtered on a Buchner filter, the solids on the filter paper are washed with demin water and dried at 60°C in a drying oven.

5.2.3 Experimental procedure

(a) Fill all reactors with 2M caustic solution, previously prepared and bring to the required temperature while agitating (not part of variables tested).

(b) Open oxygen to the reactors. Oxygen addition was not selected as a variable, so the amount added was constant according to visual bubble size, which would possibly indicate optimum agitation conditions for this system.

(c) Fill a 5 000 ml beaker with 2M caustic solution and start the agitator. Add the required amount of solids into the NaOH solution and start the pump previously set for 600 ml/min feed rate.

(d) As the beaker empties, take the next 5 000 ml beaker and add 200g of solids.

(e) Filter the continuous reactor system through a Buchner funnel connected to a vacuum pump.

(f) Store filtrate solutions and solids for washing and drying later.

(g) Continue until all the available solids are treated.

(h) Wash the residue properly with demin water until clean from entrained solution (measure the amount of demin added for wash water).

(i) Filter and dry solids (60ºC) after completion of leach and measure dry mass.

(j) Send solution and solid samples to laboratory for assaying.

(k) See analytical procedures and attachment on assays required.

(l) Test for Cu, Ni, Fe, Se, Te, Pb, As, S and PGMs.

The NaOH continuous leach test was repeated to check the repeatability of the leach. Also, there was only a limited amount of CPL solids (residue A) available, hence if anything went wrong in any one test not all the solids would have been affected.

5.2.4 Analytical procedures

In the solution samples, concentrations of copper, iron and nickel were determined by AA spectroscopy and selected samples were sent for confirmation analysis on ICP MS. Concentrations of lead, selenium, tellurium and arsenic were determined by inductively coupled plasma spectrometry (ICP-AES). The sulphate content of the solutions was determined by precipitation with BaCl and subsequent ICP analysis. Selected solution samples were also analysed for PGM contents by ICP-AES.

Solids samples were dissolved and analysed for copper, iron and nickel, lead, arsenic, selenium and tellurium content, which was determined by ICP techniques. The concentrations of sulphur were determined by the LECO analyser.

5.2.5 Calculations

Solids extraction calculations are based on the difference between initial element mass and final element mass in solids, expressed as a function of the initial element mass. Solution extraction calculations are based on the difference between initial element mass and final element mass in solution, expressed as a function of initial element mass. Calculation of sulphide sulphur and elemental S could be erroneous because the base metals in solids could be in hydroxide form and not in sulphide form. It is assumed here that all BM is in sulphide form after washing. The total sulphur content was determined with the LECO analyser. The base metals in the solids were then determined and assumed to be present in a monosulphide form, and the total sulphide sulphur was then calculated from this. This was then subtracted from the total sulphur and the total elemental sulphur was determined.

5.2.6 Mineralogy

Mineralogical analysis was done on the CPL residue from the pilot plant trial for the new BMR expansion, and it was found that copper and sulphur are the major elements present in the final residue. From the mineralogy reports, it is shown that towards the end of the CPL leach, the formation of elemental sulphur increased substantially (B period). The major minerals present in this residue were covelite, with some variation of bornite and elemental sulphur. (See table 26.)

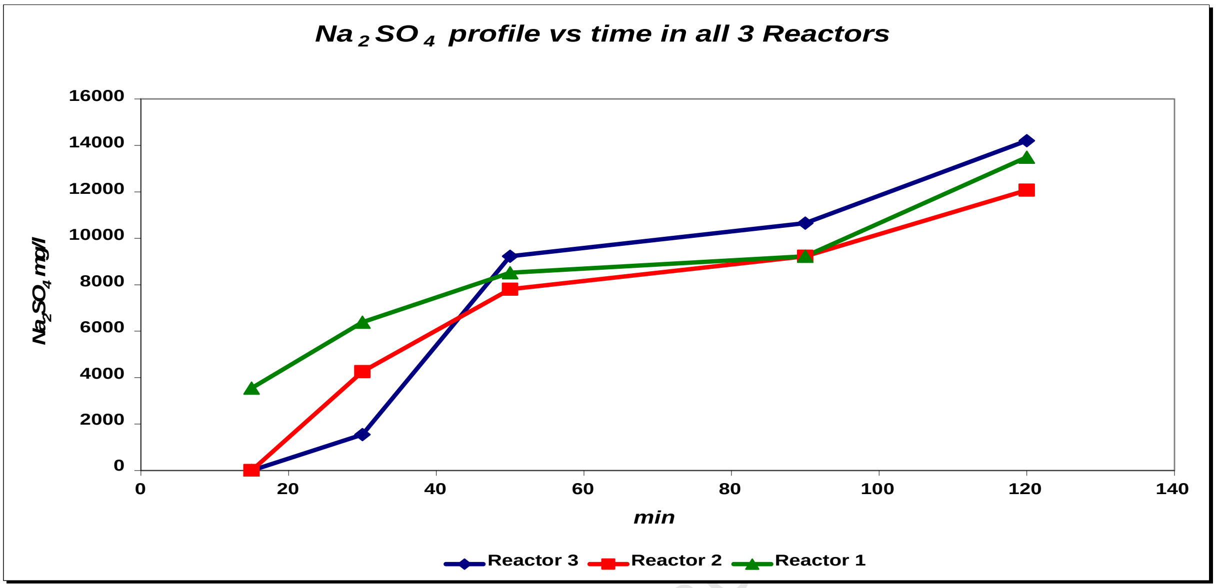
In the residue produced during the A period of this test work, covelite and bornite were also the major species present, but there was a lot less elemental sulphur. After the A residue had been treated with the NaOH leach, elemental sulphur could not be detected in the residue. In **Table 26** the major species are reported:

Species	***Residue B Mass %***	***Residue A Mass %***	***Residue A after NaOH Mass %***
Covelite (CuS)	57	79	74
Chalcanthite (CuSO4.5H_2O)	0.1	0.2	2.6
Tenorite (CuO)	0	0	16
Alt Bornite(close to Cu_3FeS_4)	4.5	7.1	3.3
Fletcherite($CuNi_2S_4$)	0.1	3.4	3.9
Sulphur(S^o)	36	10	0
Refractory	1.7	0.4	0.7

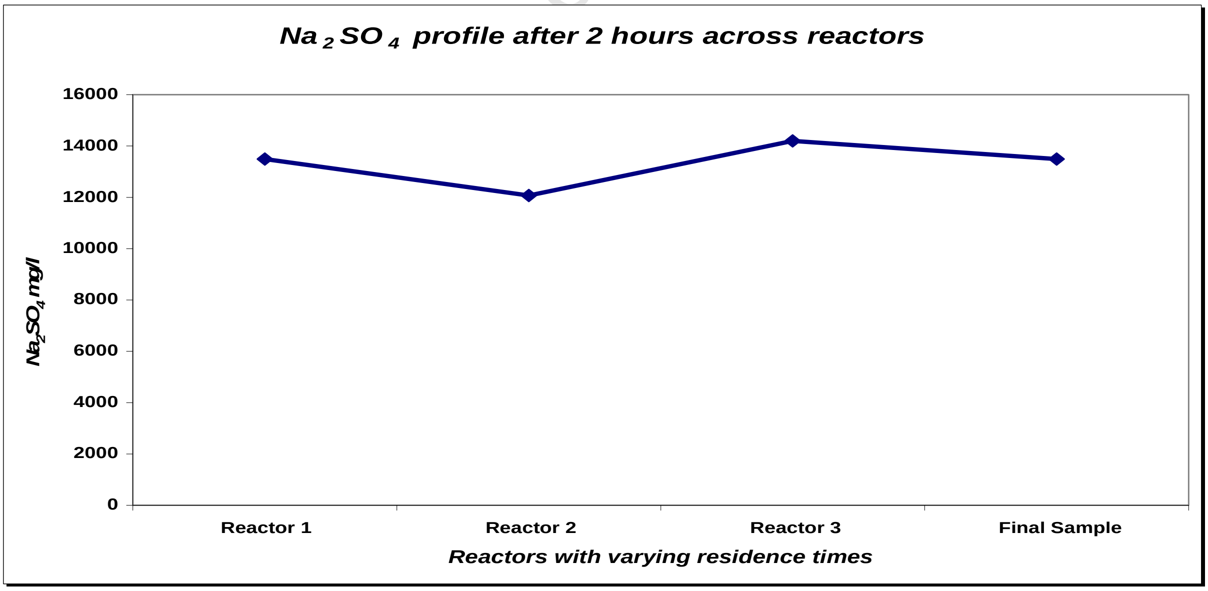
Table 26: MLA analysis of residue A, B and residue A after completion of the NaOH leach

5.3 Results and Discussion

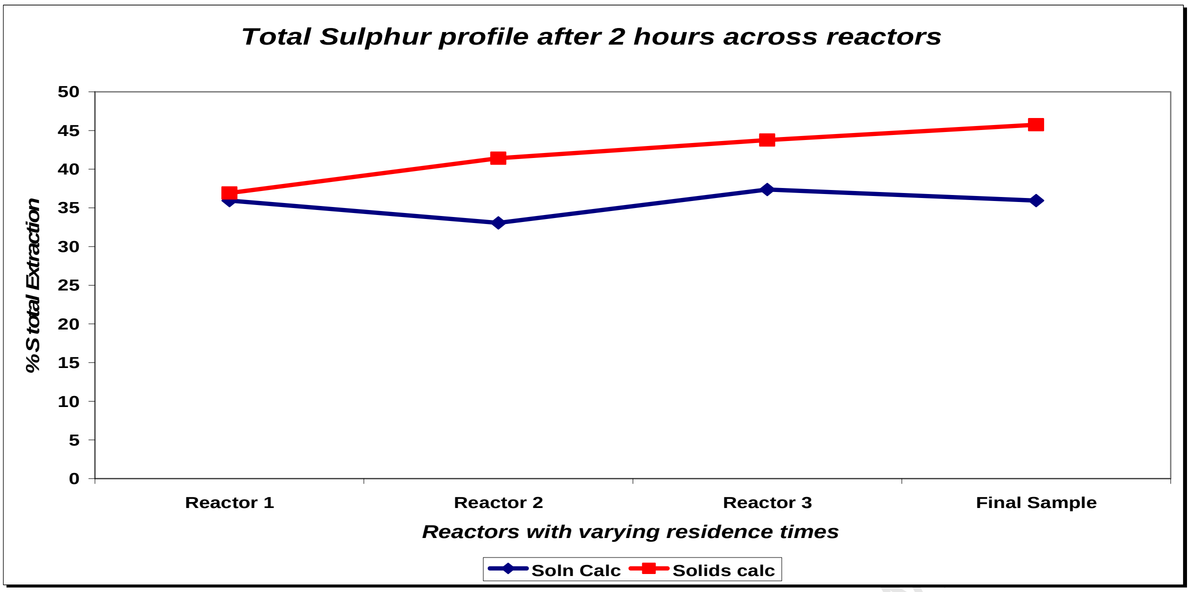
5.3.1 *Sulphur extraction*



Graph 12: Na_2SO_4 profile vs. time NaOH continuous leach



Graph 13: Na_2SO_4 profile after 2 hours in all reactors – NaOH continuous leach



Graph 14: Sulphur profile after 2 hours in all reactors – NaOH continuous leach

The sodium sulphate concentration profile across the three reactors indicates that after 15 minutes, extraction in reactor 1 was evident. After 60 minutes, in all three reactors the sodium sulphate concentrations were in the same range, indicating that the solution concentration in reaction 1 had worked through to reactor 3, although the system has not yet reached stability. The concentration profile vs. time graph shows that the sulphur concentration is going higher in all three reactors, and that even after 2 hours, it has not yet reached stability.

If the final sodium sulphate concentration in each reactor is plotted after 120 minutes, the results indicate that the sodium sulphate concentrations in all the reactors are approximately 1400mg/l. There is a spread of 15%, which can be ascribed to analytical bias.

The total sulphur extraction after 120 minutes based on solution assays were in the order of 36%. If calculating the final sulphur extraction from the solid samples taken from the reactors after 120 minutes, the results indicate that there is a slight increase in sulphur extraction (from 37% reactor 1 → 44% reactor 3). The final extraction calculated from the final solids indicates an extraction of 45%. All the elemental sulphur in this residue dissolved, but if calculating from the BM analysis, the sulphide sulphur has also been extracted between 18–20%. This correlates with the mineralogical analysis, as a 20% portion of the CuS has been changed to CuO (Tenorite) and $CuSO_4(H_2O)_5$ (Chalcanthite – copper sulphate hydrate).

The following chemical equations are proposed:

$$\mathbf{CuS + 2O_2 + 2NaOH \rightarrow Cu(OH)_2(s) + Na_2SO_4} \tag{92}$$

$$\mathbf{NiS + 2O_2 + 2NaOH \rightarrow Ni(OH)_2(s) + Na_2SO_4} \tag{93}$$

$$\mathbf{FeS + O_2 + 6NaOH \rightarrow 2Fe(OH)_3(s) + 3Na_2SO_4} \tag{94}$$

$$\mathbf{S^0 + 3/2O_2 + 2NaOH \rightarrow Na_2SO_4 + H_2O} \tag{95}$$

$$\mathbf{Cu_2Te + 2O_2 + 2NaOH \rightarrow Na_2TeO_3 + 2CuO + H_2O} \tag{96}$$

$$\mathbf{Cu_2Se + 2O_2 + 2NaOH \rightarrow Na_2SeO_3 + 2CuO + H_2O} \tag{97}$$

The yellow colour in Picture 1 below is assumed to be mainly elemental sulphur, while the blue colour is assumed to be copper. This assumption is based on analytical elemental analysis, which indicates that these two elements are the main elements extracted (See appendix 2 for results). This shows that the majority of the sulphur had been extracted within the first 27 minutes. Taking the literature[24] and the findings during the batch leach test work into account, elemental sulphur would extract with ease in a caustic solution at 80°C in the first reactor.

Picture 1: NaOH cont. leach – Reactor 1 → Reactor 3 showing solution colour after 60 min.

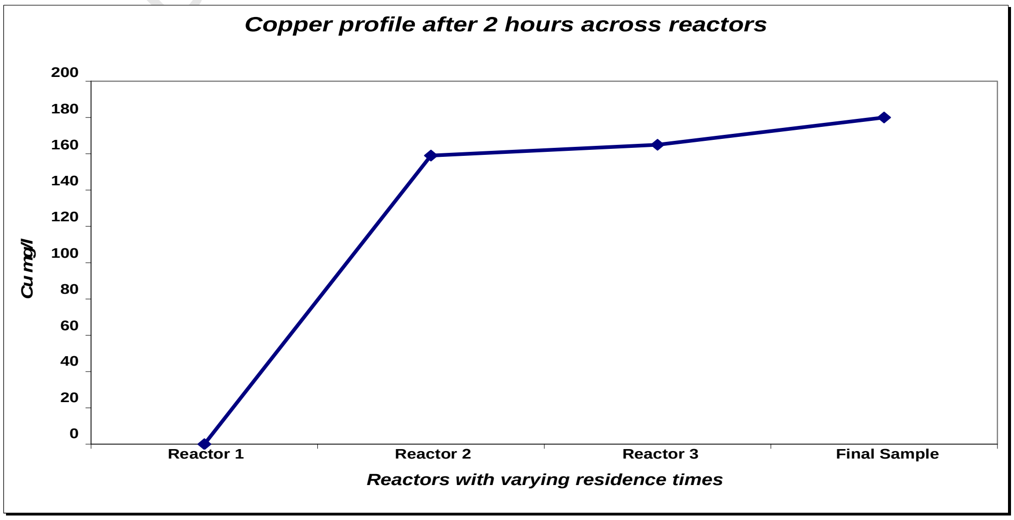
In reactor 2, sulphide sulphur starts to be attacked and extracted, and this is the reason why the blue colour is observed only from reactor 2, as the associated copper is also extracted. Copper however is reprecipitated and only a very small portion is not reprecipitated and remains in solution as an oxyanion.

Sulphur extractions between batch, NaOH 1 and NaOH 2 tests								
Batch			NaOH 1			NaOH 2		
%S_{tot}	%S^{2-}	%S^0	%S_{tot}	%S^{2-}	%S^0	%S_{tot}	%S^{2-}	%S^0
80	20	100	45	19	100	45	19	100

Table 27: Sulphur extraction summary on NaOH batch and continuous leach

The batch experiments, as explained in section 4.3 and 4.4, were performed on a different residue. The results reported in **Table 27** were for the batch leach tests performed at 80°C, and the results obtained after two hours in the continuous tests. There were no difference in conditions between continuous test 1 and 2, and the only reason for duplicating the leach was to see if the results would be consistent. As can be observed from Table 27, the results are fairly consistent across all of the tests, and only the batch test which had a different residue had a lot more elemental sulphur present initially. This definitely shows that all elemental sulphur had been extracted, while some 20% of the sulphide sulphur portion had been extracted as well in 60 minutes. The results are consistent with the literature, as under the atmospheric leaching conditions, all elemental sulphur dissolved, while a portion of the sulphide sulphur was also attacked.

5.3.2 *Base Metal extraction (Cu, Ni, Fe)*



Graph 15: Copper profile after 2 hours in reactors – NaOH continuous leach

Copper is extracted from the residue and it is definitely residence time related, as it only starts extracting in reactor 2. The extraction however is only 1.13%. Nickel, iron and cobalt do not solubilise at all, and the data shows no extraction of these elements. As can be observed from **Table 28**, there is a variation in results between the tests and there definitely is copper dissolution, as even though this dissolution is very low, it still results in a blue colouration of the solution. From the mineralogical analysis conducted on the leach residue, it is shown that most of the residue consists of CuS and approximately 18% of this was converted to CuO and $CuSO_4(H_2O)_5$. It was suspected from reactions 98–104 in the literature[11 & 19], that copper would have been converted to the hydroxide form and it is strange that 18% has been converted to the oxide form. It is therefore suggested that some derivative of **reaction 103** is taking place[19], and thus that the copper in solution is an oxyanion of copper, possibly $Cu(OH)_4^-$ [24]. The following reactions are proposed to have happened during the caustic leach:

$$\mathrm{CuS + 2O_2 + 2NaOH \rightarrow Cu(OH)_2(s) + Na_2SO_4} \tag{98}$$

$$\mathrm{NiS + 2O_2 + 2NaOH \rightarrow Ni(OH)_2(s) + Na_2SO_4} \tag{99}$$

$$\mathrm{FeS + O_2 + 6NaOH \rightarrow 2Fe(OH)_3(aq) + 3Na_2SO_4} \tag{100}$$

$$\mathrm{Cu_2Se(s) + 2NaOH + 2O_2 + H_2O \rightarrow Na_2SeO_3 + 2Cu(OH)_2} \tag{101}$$

$$\mathrm{Cu_2Te(s) + 2NaOH + 2O_2 + H_2O \rightarrow Na_2TeO_3 + 2Cu(OH)_2} \tag{102}$$

Alternative:

$$\mathrm{2Cu_2Te(s) + 4NaOH + 3O_2 \rightarrow 2Na_2TeO_3 + 2Cu_2O + 2\,H_2O} \tag{103}$$

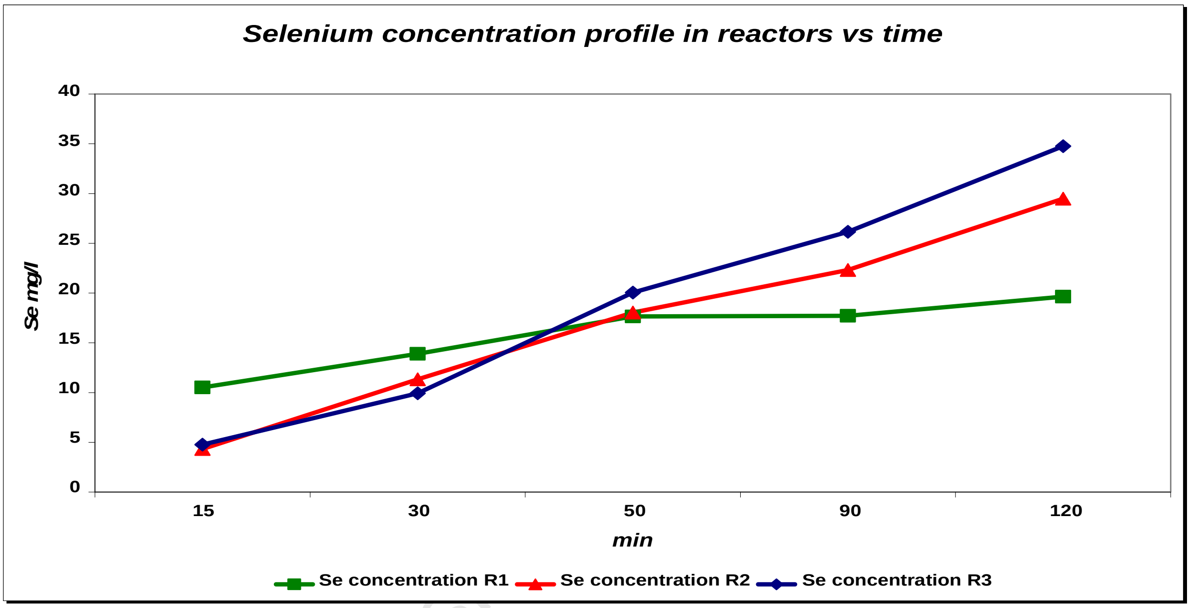
$$\mathrm{Cu_2Te + 2O_2 + 2NaOH \rightarrow Na_2TeO_3 + 2CuO + H_2O} \tag{104}$$

Referring to **Picture 1**, it is clear that copper only starts solubilising in reactor 2, ie after 27 minutes, and it is presumed that this is when the sulphide sulphur is being attacked as well. It is proposed that only after the elemental sulphur has all been oxidised, does the attack on sulphide sulphur start, and a small portion of the associated copper is not converted to the hydroxide form, but remains in solution as the oxyanion.

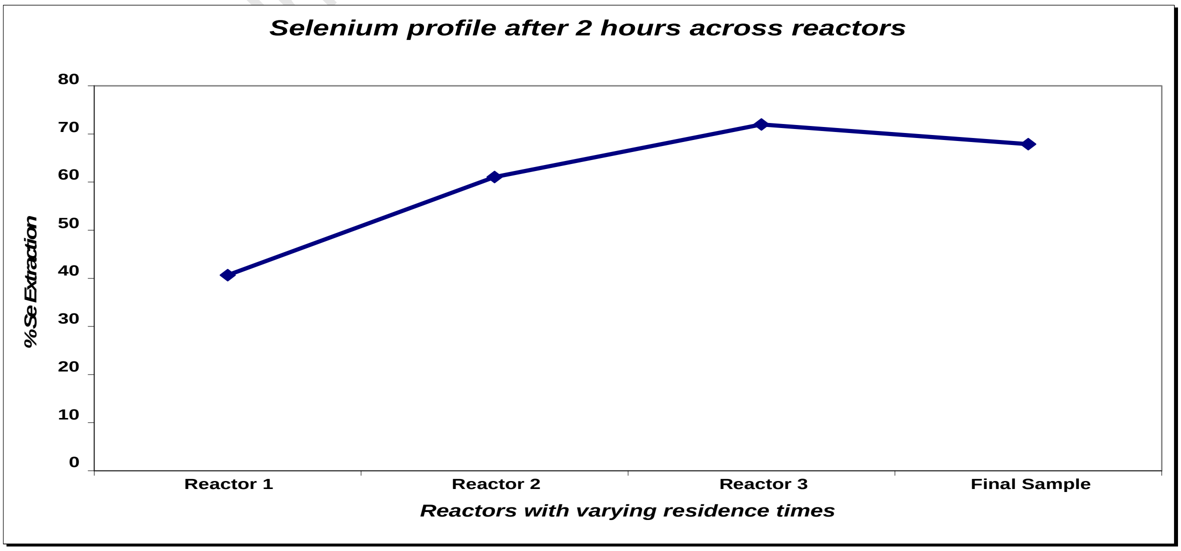
Copper extractions between batch, NaOH 1 & NaOH 2 tests		
Batch	***NaOH 1***	***NaOH 2***
%Solution extraction	%Solution extraction	%Solution extraction
0.9	1.96	1.1

Table 28: Copper extractions between batch and continuous leaches

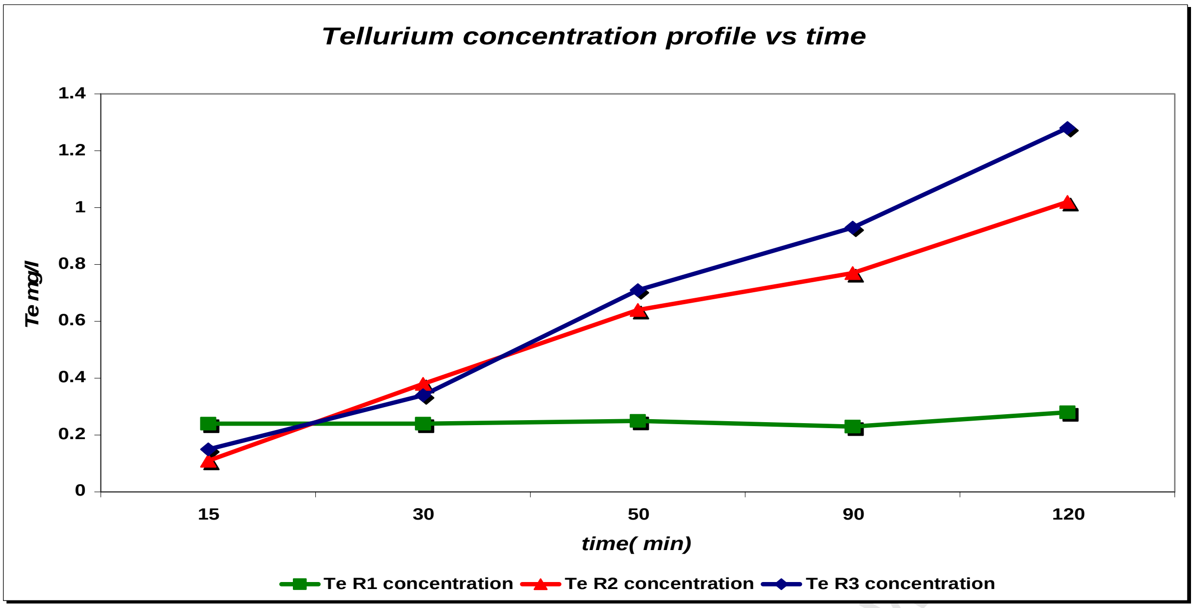
5.3.3 Selenium and tellurium extraction



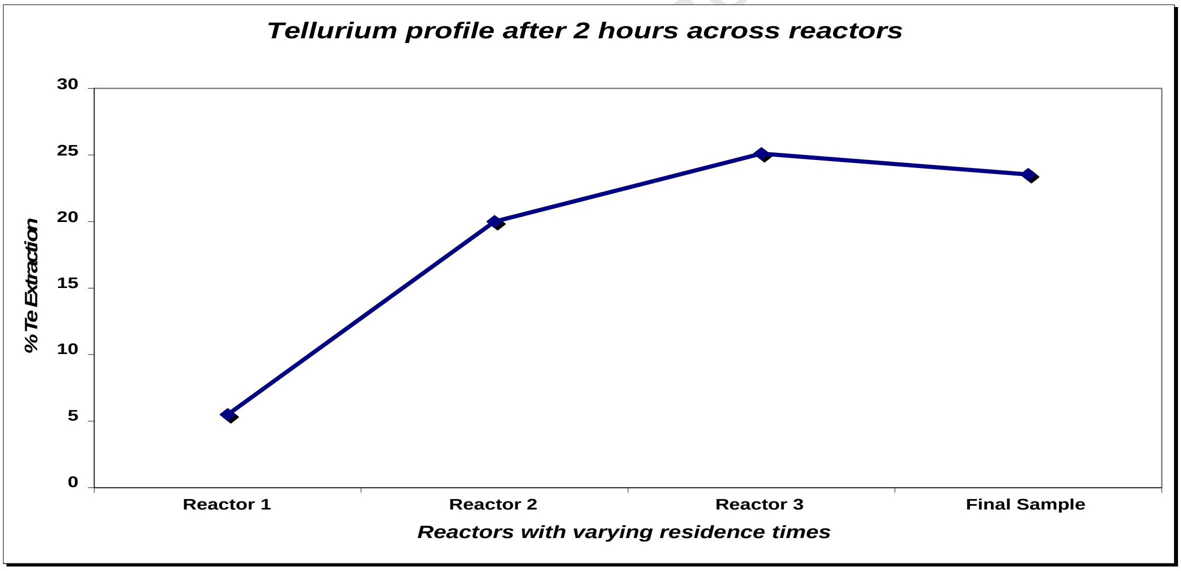
Graph 16: Se concentration in 3 reactors after 2 hours – NaOH continuous leach



Graph 17: Se extraction profile after 2 hrs in reactors – NaOH continuous leach



Graph 18: Te concentration profile across reactors after 2 hrs – NaOH continuous leach



Graph 19: Te extraction profile after 2 hrs – NaOH continuous leach

The concentration profile vs. time graph shows that the selenium concentration is increasing in all 3 reactors, and that even after 2 hours, it has not yet reached stability. Selenium extraction is not time-related as has been proven by the batch leach tests, but the selenium extraction profile across the individual reactors indicates that this might well be the case. Both were done at a solids loading of 50g/l, so why these differences between the batch and continuous tests is experienced, is not understood. A possible explanation is that different residues were used for the batch tests (PLR) and continuous tests (CPL A), and it is more likely that Se in the PLR residue existed more as a Cu_2Se, which will extract more easily than if Se existed as Ag_2Se, which would not extract under these conditions[24]. Selenium extraction does not seem to reach stability after the mean average residence time (60 min), and after the 3rd reactor reached 72% extraction. A longer residence time might show a better extraction, but if it existed as Ag_2Se, this is doubtful. The mineralogical results indicate that selenium forms onto the edges of the Pt core alloy platelets and onto a Pd-Au-Cu alloy. It is not clear if the soluble Se exists as the selenite species or as the selenate species, but with this high residence time and caustic strength, possibly as a selenate. It is, however, also possible to exist as a selenite **(reaction 107)** because CuO is one of the species noticed in the mineralogy of the residue[26]. Decreasing the residence time to 20 minutes would inhibit extraction of Se.

The following are possible reactions which could happen with the Se, and it would be impossible to give a definite reaction as the individual Se species were not identified. **Reaction 109** will only happen at much higher temperatures.

$$2Se + 4NaOH + 3O_2 \rightarrow 2Na_2SeO_4 + 2H_2O \qquad (105)$$

$$Se(s) + 2NaOH + O_2 \rightarrow Na_2SeO_3 + H_2O \qquad (106)$$

$$Cu_2Se + 2O_2 + 2NaOH \rightarrow Na_2SeO_3 + 2CuO + H_2O \qquad (107)$$

$$Cu_2Se(s) + 2NaOH + 2O_2 + H_2O \rightarrow Na_2SeO_3 + 2Cu(OH)_2 \qquad (108)$$

$$Ag_2Se(s) + 2NaOH + O_2 \rightarrow Na_2SeO_3 + 2Ag + H_2O \qquad (109)$$

The concentration profile vs. time graph shows that the tellurium concentration is increasing in reactors 2 and 3, but not in reactor 1. This indicates that no extraction occurs in reactor 1, but extraction appears to start from reactor 2. Tellurium extraction does not reach stability after the mean average residence time (60 min) and after the 3rd reactor, an extraction of 25% was obtained. A longer residence time might show a better extraction. Assay results on tellurium were, however, extremely low and probably very close to the detection limit in order to draw any firm conclusions. As with Se, the speciation of Te was not done, therefore a reaction mechanism cannot be proposed with any certainty. The Te in solution would exist as tellurite, simply because tellurate would precipitate in strong caustic concentrations as with this test. **Reaction 111, 112** and **113** are all possible as copper oxide was noticed in the residue after doing the mineralogy on the residue.

$$2Te + 4NaOH + 3O_2 \rightarrow 2Na_2TeO_4 + H_2O \qquad (110)$$

$$Cu_2Te + 2O_2 + 2NaOH \rightarrow Na_2TeO_3 + 2CuO + H_2O \qquad (111)$$

$$2Cu_2Te(s) + 4NaOH + 3O_2 \rightarrow 2Na_2TeO_3 + 2Cu_2O + 2H_2O \qquad (112)$$

$$Cu_2Te(s) + 2NaOH + 2O_2 + H_2O \rightarrow Na_2TeO_3 + 2Cu(OH)_2 \qquad (113)$$

It is clear from the literature survey that Se and Te are elements whose dissolution rates are not only strongly temperature dependant, but also very dependant on oxygen partial pressure. At the conditions this test work was done at, selenium extraction would be very time dependent; longer leach times would predict better Se extraction and possibly to a large extent[19], in the selenite form. Extractions in the order of 50–70% could possibly be better if the leach time were longer. **Reactions 111–113** would most likely be the chemistry which can be associated with this test work. Selenium would almost certainly be present as a copper selenide and a silver selenide in the CPL residue. The copper selenide would form copper oxide and copper hydroxide in the caustic leach under the conditions tested, which can be seen from the mineralogy. The silver selenide from literature would not dissolve under the conditions tested, which would probably account for the remainder of the selenium not extracted.

Tellurium , according to the literature, is extremely time related, which would make it likely to extract within the first 20 minutes; any longer and the Te would be converted to the tellurate form. However, the findings from this test work indicate that tellurium does not extract within the first 27 minutes, which is the residence time in reactor 1, but starts to extract only from reactor 2. Tellurium would exist as tellurite, because tellurate is insoluble in this caustic strength solution[1].

Selenium extractions between batch, NaOH 1 & NaOH 2 tests					
Batch		***NaOH 1***		***NaOH 2***	
Solution % Extraction	***Solids % Extraction***	***Solution % Extraction***	***Solids % Extraction***	***Solution % Extraction***	***Solids % Extraction***
86%	85%	57%	53%	72%	53%

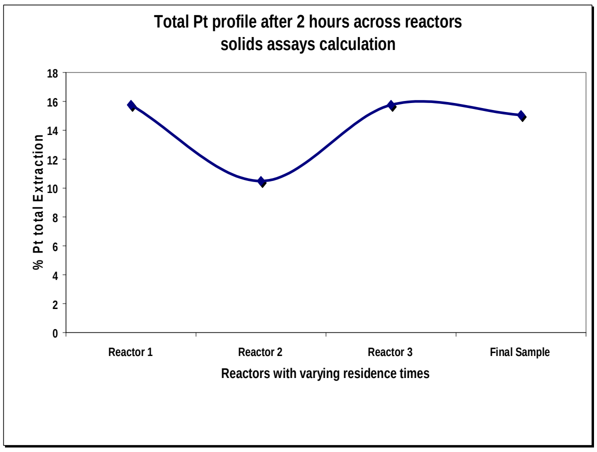
Tellurium extractions between batch, NaOH 1 & NaOH 2 tests					
Batch		*NaOH 1*		*NaOH 2*	
Solution % Extraction	*Solids % Extraction*	*Solution % Extraction*	*Solids % Extraction*	*Solution % Extraction*	*Solids % Extraction*
57%	33%	13%	19%	24%	19%

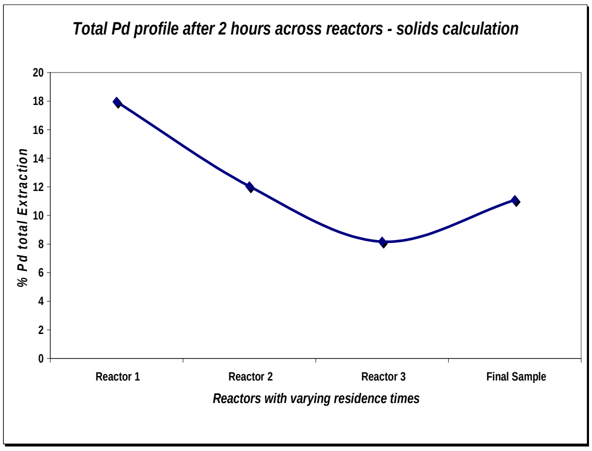
Table 29: Selenium and Tellurium extractions on all of the caustic leaches

5.3.4 PGM extraction

In test work done by employing a caustic atmospheric leach with oxygen, the dissolution of Pt increased as the NaOH concentration (0.25M) and temperature increased, up to 35% Pt dissolution at 80°C. At 50°C, the Pt dissolution was 0.2%. A major concern with caustic leaches is the dissolution of PGMs and base metals under atmospheric conditions. The atmospheric caustic leach conditions can be adjusted (lower temperature and NaOH concentration) to minimise PGM dissolution[11]. In a high temperature, high pressure and similar caustic concentration leach, the products of a SO_2 reduction step are Se and PtSe in sulphuric acid media. All other elements were removed from the residue by other leaching steps. For all the PGMs, dissolution was minimal.[4] In another high temperature, high pressure and varying caustic concentration leach programme, the aim was to remove sulphur and selenium in a final PGM concentrate to acceptable levels. The use of higher strength caustic solutions (3N), at 150°C and 200°C, resulted in some leaching of Pt, but Ru dissolution was very high. The weaker strength of caustic solution of 0.5 N did not result in measurable precious metal solubilisation.[26] In an atmospheric leach test programme with 2M NaOH at 80°C, but using no oxygen, PGM dissolution was minimal.[10].

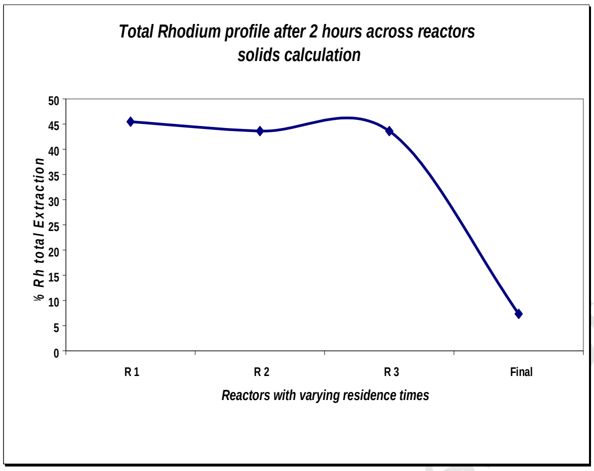
SECTION 5 CAUSTIC CONTINUOUS LEACH

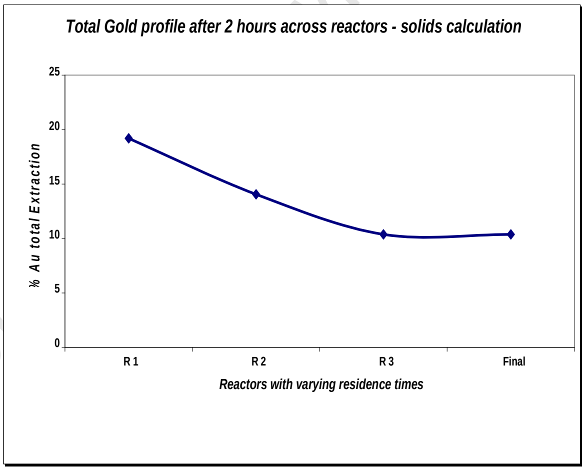




Graph 20: Pt profile in NaOH continuous leach

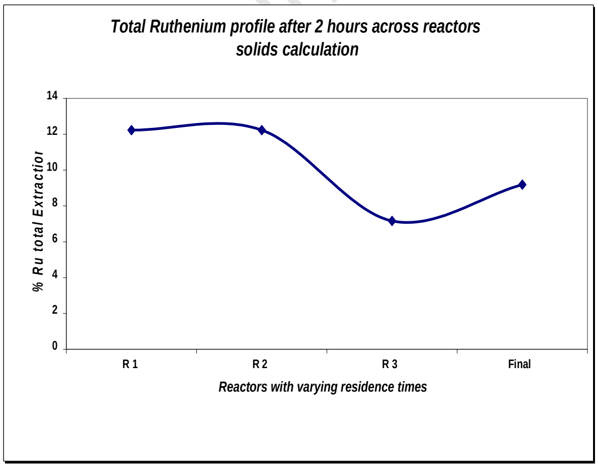
Graph 21: Pd profile in NaOH continuous leach

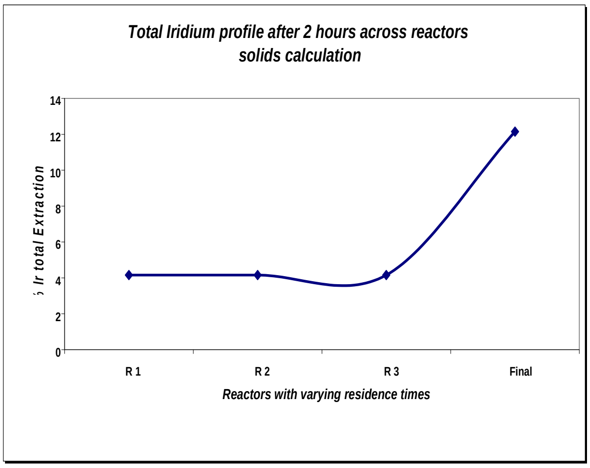




Graph 22: Rh profile in NaOH continuous leach

Graph 23: Au profile in NaOH continuous leach





Graph 24: Ru profile in NaOH continuous leach

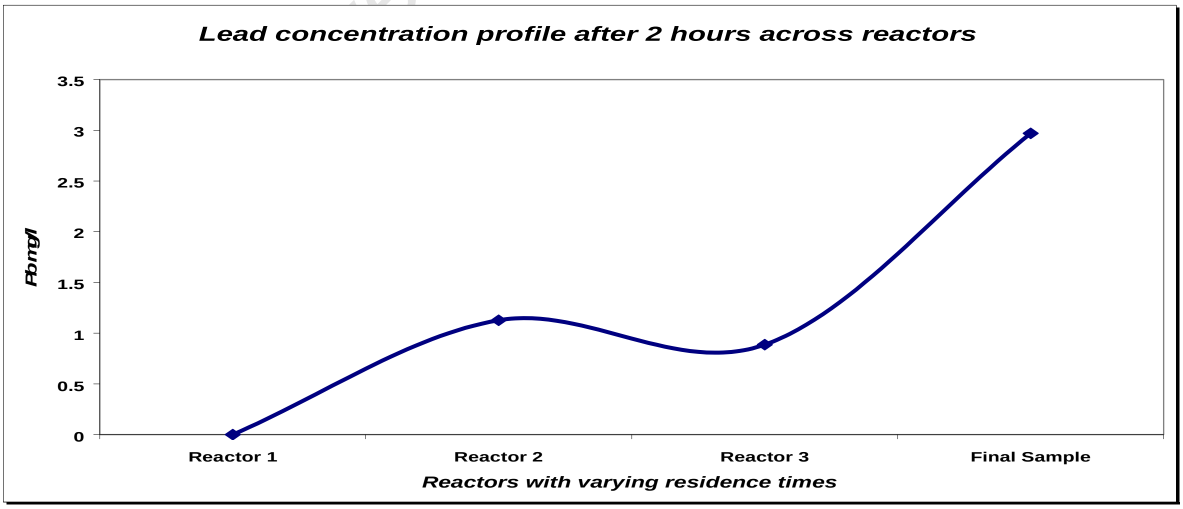
Graph 25: Ir profile in NaOH continuous

PGM extractions between NaOH 1 & NaOH 2 tests				
Element	***NaOH 1***		***NaOH 2***	
	Solution % Extraction	***Solids % Extraction***	***Solution % Extraction***	***Solids % Extraction***
Pt	N/A	14%	0%	15%
Pd	N/A	10%	0%	11%
Rh	N/A	7%	0%	7%
Au	N/A	10%	0%	10%
Ru	N/A	8%	0%	9%
Ir	N/A	11%	0%	12%

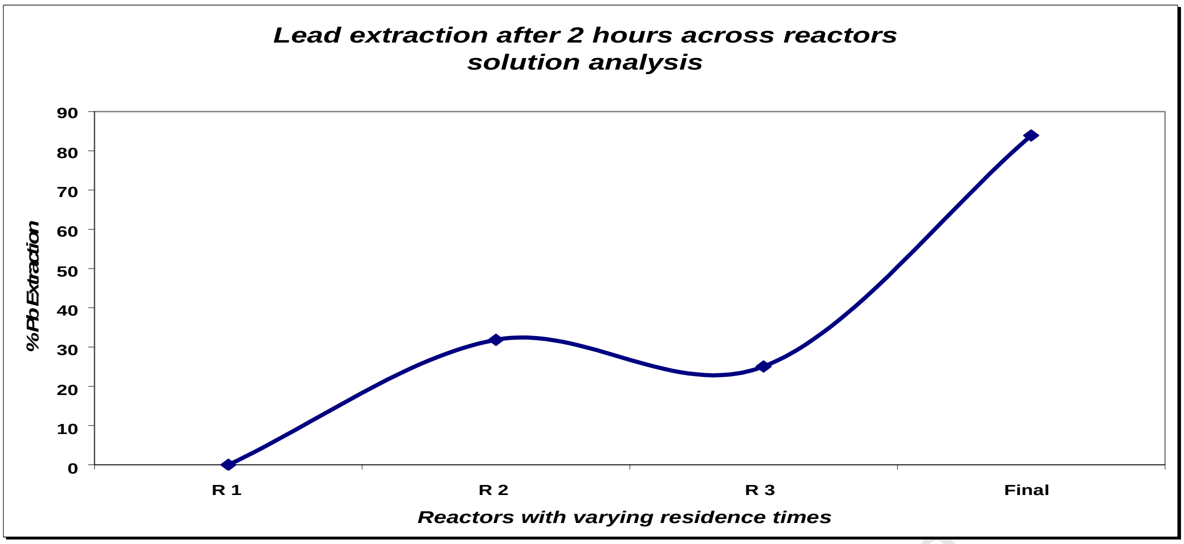
Table 30: PGM extractions in NaOH continuous leach

Graphs 20–25 indicate that there was PGM extraction based on solids assay calculations. However, it must be emphasised, based on solution assays done on the ICP MS, PGM dissolution was non-existent. The literature available indicates that PGM solubilisation under atmospheric conditions or slight overpressure could be temperature dependant. Under pressure conditions, minimal dissolution of PGMs seems to occur at approximately 1M caustic strength. These tests were performed at a 2M caustic strength, which is high, and by possibly lowering this, extraction of PGMs would be minimal, if any were indeed extracted.

5.3.5 *Pb extractions*



Graph 26: Pb concentration profile after 2 hrs – NaOH continuous leach



Graph 27: Extraction profile after 2 hrs – NaOH continuous leach

In the batch leach tests, no lead was extracted under the above conditions, and it does appear as if lead extraction in 2M caustic solution is temperature dependant, with the low temperatures resulting in some lead extraction. However, from the continuous trials, indications are from even the very low assay results that lead extraction does occur. After the 3rd reactor, 25% Pb was extracted, and the final solution assays seem to indicate an extraction of as much as 80%. Lead concentration in all the assays was extremely low and no firm conclusions can be drawn from the results.

From the literature[24], when sulphur is removed, which happens in reactor 1, selective alkaline leaching exploits the differences in the relative stability of the various oxyanions in concentrated NaOH solutions. As indicated by mineralogical data, a portion of the base metals is converted to its oxide and hydroxide forms, which could also result in lead hydroxide being formed in reactor 1, and then converted to an oxyanion

$$PbO + 2\,NaOH + H_2O \rightarrow Na_2Pb(OH)_4(aq) \qquad (114)$$

$$PbSO_4 + 2NaOH \rightarrow Pb(OH)_2(s) + Na_2SO_4 \qquad (115)$$

$$Pb(OH)_2(s) + OH^- \rightarrow HPbO_2^- + H_2O \qquad (116)$$

Under the conditions the leach was conducted, Pb could exist as a soluble oxyanion. This would then provide the opportunity to remove lead, which is based on the differential solubility of the oxyanions of lead. When lead exists as Pb(II), it is present as $HPbO_2^-$ ion in concentrated caustic solution, but if oxidised to Pb(IV), its solubility is significantly reduced. The literature indicates that some lead oxide solubilises at high hydroxide concentrations and is stable as the $HPbO_2^-$ ion. It is therefore suggested that the above takes place, resulting in some significant lead extraction, although the assay results were too low to quantify this with any accuracy.

Pb extractions between NaOH 1 & NaOH 2 tests				
Element	***NaOH 1***		***NaOH 2***	
	Solution % Extraction	***Solids % Extraction***	***Solution % Extraction***	***Solids % Extraction***
Pb	80%	55%	25%	56%

Table 31: Pb extraction in continuous NaOH leach

5.4 Conclusions

The main objective of the NaOH leach is to test if the CPL residue can be treated on a continuous basis, in order to extract as much of the elemental sulphur as possible. This has been achieved with success, as elemental sulphur is dissolved reasonably quickly within the first 27 minutes. From the test trial it is clear that the sulphides are attacked, but only starting in reactor 2, which appears to be when all the elemental sulphur has been oxidised to sulphate. When the sulphides start to dissolve, it converts the copper, nickel and iron to the hydroxide form, which is not soluble. However, a very small portion of copper (1–2%) did not precipitate as a hydroxide, but stayed soluble as an oxyanion $Cu(OH)_4^-$.

Selenium was dissolved in reactor 1 up to 40%, which is after 27 minutes, and dissolution continued to increase to 70% in the final reactor (60 minutes). Contrary to the batch leach tests, which show that Se dissolution is not residence time related, it is clear from the continuous tests this is in fact the case and further that selenium extraction could have been better if the residence time were longer.

Tellurium extraction did not extract in reactor 1, which shows that this element only starts extraction possibly when the sulphides starts to extract. Again, this is an anomaly when compared to the literature, which states that tellurium under the test conditions of the continuous trial (but in batch, with pO_2 at 65kPa, and not truly atmospheric), should have dissolved as a tellurite species within the first 20 minutes. Tellurium as a tellurate species should precipitate, which does not appear to happen here. Tellurium possibly would have yielded better extraction results had the residence been longer than 60 minutes.

PGM extraction appears to be minimal if extraction results were calculated from solution extractions. No PGMs could be detected via the ICP MS analyser. From the literature survey, however, the indications are that Pt would be soluble under atmospheric conditions. The fact that minimal PGM extraction occurs is very positive because this would simplify the treatment of the effluent stream.

Pb dissolution is also extremely positive as this will be an element which would present a problem if aiming to treat this residue in the PMR. There was no Pb dissolution in reactor 1, but dissolution increased to 30% in reactors 2 and 3. The final sample, which was analysed by a different laboratory by ICP MS, indicated an extraction of lead in the final reactor of as much as 80%. The literature indicates that lead will be soluble as an oxyanion ($HPbO_2^-$) and when oxidised to the Pb(IV) species, it would be insoluble in NaOH solution. The batch tests showed no Pb dissolution, however this is shown by the continuous tests, which cannot be explained. It would be suspected that Pb would be oxidised to the Pb(IV) species, under the oxidising conditions which existed in the continuous trial and then precipitated. Pb only starts dissolving once the elemental sulphur has been oxidised, ie when the sulphide attack starts. The percentage mass losses in both NaOH tests were 20.0% and 20.7%, which correlates extremely well with the calculated extractions from the analytical results.

If the only aim of the NaOH leach was to oxidise any elemental sulphur, the continuous trial showed this could be accomplished very successfully within the first reactor, ie within 27 minutes. From literature this could be done without oxygen as well. Silica would also be extracted under these conditions with a reasonable amount of success, when no oxygen is added, as proven in previous work done. If thereafter, ie starting from reactor 2, oxygen addition to the leach can be implemented and caustic concentrations can be optimised, possibly much better extractions results can be achieved for Se, Te and Pb. Unfortunately, caustic concentrations and pHs in the different reactors were not measured.

It is therefore proposed that test work could be continued to test the effects of this.

SECTION 6

COPPER OXIDATIVE POLISHING PRESSURE LEACH

6.1 Introduction and Objectives

As described in the introduction section, in the course of finding a suitable process for treating the new copper pressure leach residue, a test programme was initiated to fulfil this requirement. The main objective was to treat this residue in such a manner as to separate the PGMs from all the other elements and to send this concentrated PGM residue directly to the PMR for further treatment.

The test work then started with NaOH batch leach tests in order to determine the optimum conditions under which the A residue can be processed so that it contains as little elemental S as possible. This was then followed with a continuous NaOH leach where the residue from Period A was treated under the conditions proposed in the NaOH batch leach tests. This was largely successful in removing not only elemental S, but other unwanted elements from the residue. The caustic leach, however, did not remove the major base metals like copper, as it was not the aim to do so, but presented a residue which could hopefully be upgraded with a sulphuric acid leach.

Therefore, the objective for this test work phase is to test copper, nickel, iron, sulphur, PGMs, tellurium and selenium dissolution under varying conditions of temperature, pressure, oxygen partial pressure and acid conditions.

The aim of testing this leach under varying conditions is to test and propose a process which would be used in order to extract these. Other impurities such as lead would also be measured in order to establish a baseline for further test work, and to treat this residue within Anglo Platinum, rather than toll refine it.

6.2 Materials and Methods

6.2.1 Experimental programme

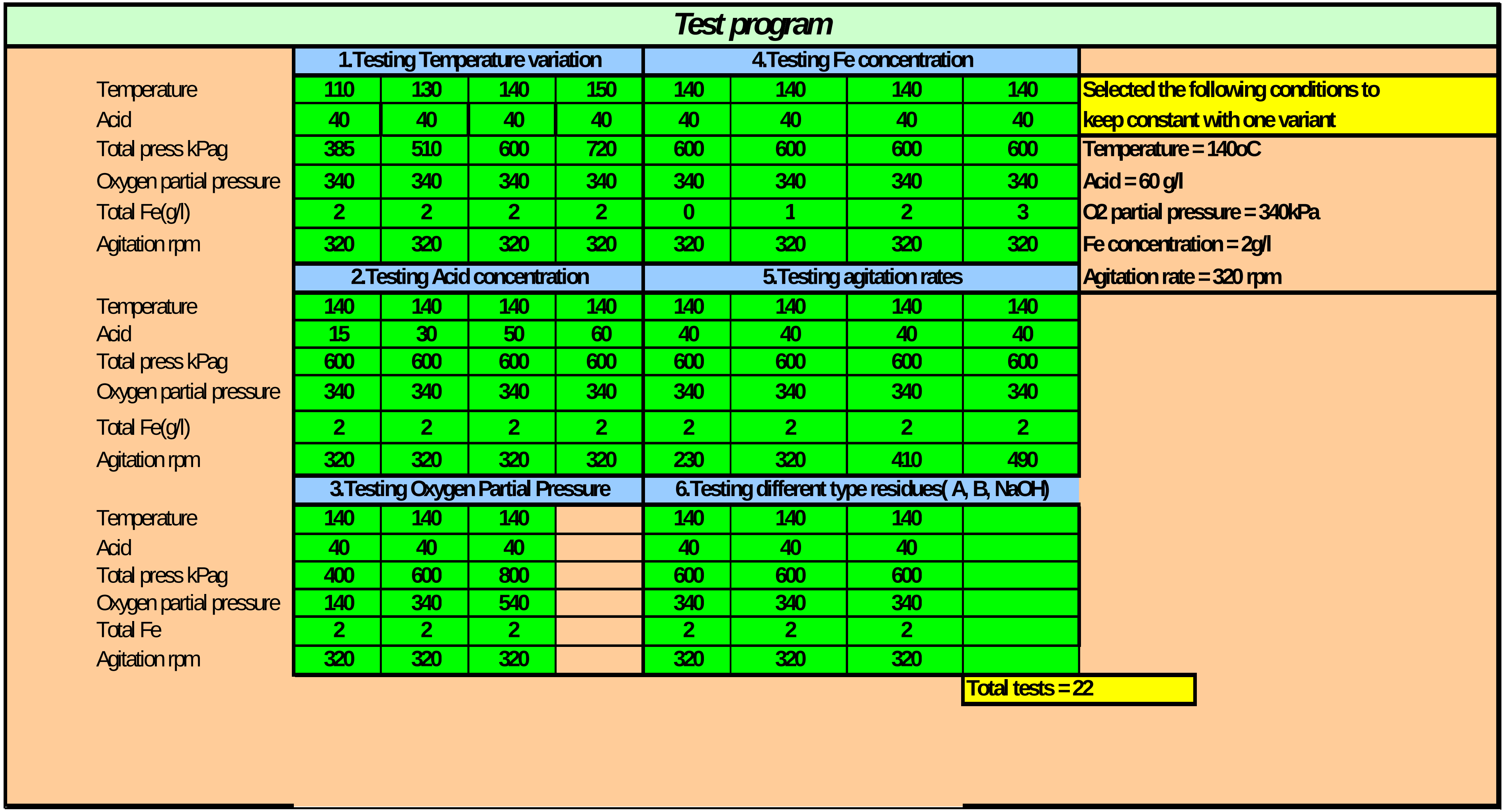
Conditions to vary

Temperature : 110^{o}C, 130^{o}C, 140^{o}C, 150^{o}C
Oxygen partial Pressure : 140, 340, 540 kPa
Acidity : 15 g/l, 30g/l, 50g/l, 60g/l
Total Fe as Fe^{2+} : 0g/l, 1g/l, 2g/l, 3 g/l
Agitator rpm : 200, 280, 360, 440 rpm
Solids : 10g/l

The base case will be:

Temperature : 140^{o}C
Oxygen partial Pressure : 340 kPa
Acidity : 30g/l
Total Fe as Fe^{2+} : 2g/l
Agitator rpm : 280 rpm
Solids : 10g/l

Each variation was tested, resulting in 22 tests. For each variation, element extraction is then plotted vs. time. Another four tests were done using a concentration of approximately 200g/l sodium sulphite in order to determine the influence of the agitator on the oxygen mass transfer rate and the mass transfer coefficient of the reactor. On all the graphs presented, the last result on the time scale represents the final solution sample taken after the leach solution was cooled and removed from the autoclave



Test program

	1.Testing Temperature variation				4.Testing Fe concentration				
Temperature	110	130	140	150	140	140	140	140	Selected the following conditions to
Acid	40	40	40	40	40	40	40	40	keep constant with one variant
Total press kPag	385	510	600	720	600	600	600	600	Temperature = 140oC
Oxygen partial pressure	340	340	340	340	340	340	340	340	Acid = 60 g/l
Total Fe(g/l)	2	2	2	2	0	1	2	3	O2 partial pressure = 340kPa
Agitation rpm	320	320	320	320	320	320	320	320	Fe concentration = 2g/l
	2.Testing Acid concentration				5.Testing agitation rates				Agitation rate = 320 rpm
Temperature	140	140	140	140	140	140	140	140	
Acid	15	30	50	60	40	40	40	40	
Total press kPag	600	600	600	600	600	600	600	600	
Oxygen partial pressure	340	340	340	340	340	340	340	340	
Total Fe(g/l)	2	2	2	2	2	2	2	2	
Agitation rpm	320	320	320	320	230	320	410	490	
	3.Testing Oxygen Partial Pressure				6.Testing different type residues(A, B, NaOH)				
Temperature	140	140	140		140	140	140		
Acid	40	40	40		40	40	40		
Total press kPag	400	600	800		600	600	600		
Oxygen partial pressure	140	340	540		340	340	340		
Total Fe	2	2	2		2	2	2		
Agitation rpm	320	320	320		320	320	320		

Total tests = 22

Table 32: Experimental programme for sulphuric acid pressure leaching tests

6.2.2 *Feed Materials*

Solid residue from NaOH leach

	Res A	***Res B***	***NaOH leach***
Element	***Assay (g/t & %)***	***Assay (g/t & %)***	***Assay (g/t & %)***
Cu %	53.29	37.75	61.09
Ni %	1.57	1.5	1.96
Fe %	0.1	1.76	0.18
Co %	580	320	630
S %	37.1	57.25	25.37
S^0	9.3	36.4	0
Pt	45.2	105	48.4
Pd	819	2150	918
Rh	42.2	78	49.3
Au	108	287	122
Ru	47	128	53.8
Ir	14.9	35.4	16.5
Se	1610	1793	946
Te	170	302	173
Pb	118	333	65.9
As	115	132	81.1
Sn	58.3	56	44.7
Mn	<0.02%	<0.02	<0.02
Bi	6.56	14.7	7.7
Sb	55.5	89.5	53.4
SiO_2	NA	NA	NA

Table 33: Comparison between residues after NaOH continuous leach

Sulphuric acid 98% AR

- Defrothers – Bevaloid

Note – Tests to be done without any ligno-sulphonate

- Oxygen cylinders

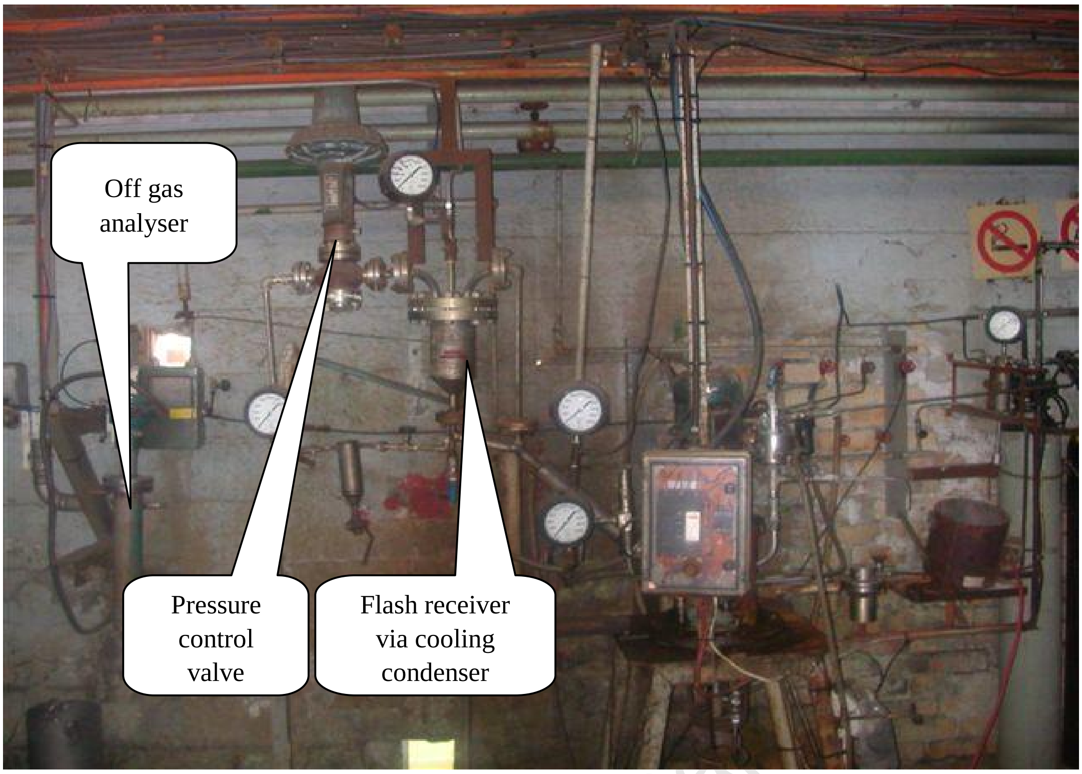
- Ferrous sulphate crystals
- Demin water

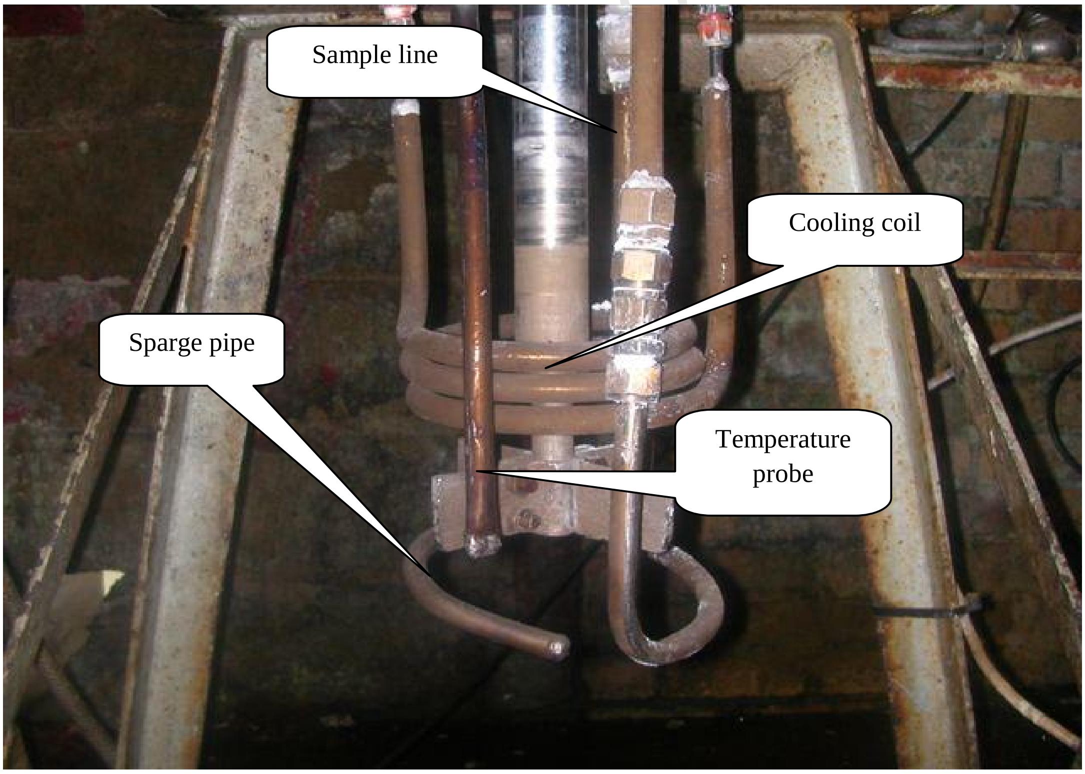
Sodium Sulphite test

- Na_2SO_3 at approximately 200g/l concentration, about 90 liters of solution

6.2.3 Equipment

A carpenter steel autoclave with a 7litre operating volume was used. This autoclave is fitted with an agitator with an axial impeller 7.6 cm in diameter and a variable speed drive on the motor. A mechanical seal using water is fitted on the agitator shaft. Oxygen is added from a cylinder through a rotameter, which controls the oxygen flow, into the autoclave via a sparge tube beneath the impellers. The off gas from the autoclave goes via a jacketed cooling condenser to a flash tank. The flash tank can be drained periodically if necessary and the off gas from the flash tank is controlled with a pressure control valve, in order to control the pressure in the autoclave to a set point. The off gas is measured for oxygen content with an oxygen analyser. The autoclave is heated with an electric jacket surrounding the outside of the autoclave shell and the temperature is controlled to set point automatically. Finer temperature adjustment can be achieved with the cooling coil that is fitted on the inside of the autoclave. This is also used for quicker cooling of the contents on discharge. The autoclave is fitted with a sampling point beneath the slurry line and a sampling vessel of volumetric capacity of 200 ml, from which samples can be taken with the autoclave under pressure. This was also used for charging acid into the vessel while under pressure, and for recharging the solids portion from the samples taken. Samples were filtered through a Millipore filter (0.45 micron) fitted to a vacuum pump and the redox was measured of the sample taken.





Picture 2: Pictures of autoclave set up

6.2.4 Experimental procedures

The autoclave was filled to 7 litres with demineralised water, and 70 g of the residue from the NaOH leach were weighed out and put into the autoclave to give 10g/L solids loading. The required amount of ferrous sulphate crystals were weighed and added to the autoclave contents. The autoclave was filled with nitrogen gas to a $100kPa_g$ pressure and the agitator seal pump started. The agitator was started after the correct agitator speed was selected. Only at this stage was the heating jacket switched on and the contents heated to the required temperature. When the temperature was above 120°C, the pressure was increased to the required set point, with nitrogen gas. A sample of the slurry was taken at this stage. The oxygen was now opened to the vessel, and when the oxygen in the off gas reached 95%, another sample was taken. The required amount of acid was added to the vessel through the sampling point, and this was done in stages with the acid content in diluted form. The leach continued for 4–5 hours, and regular samples were taken. The initial tests were done for a 240minute period, but it was later realised that complete extractions were not achieved, and the leaching period were increased to 300min. Solution samples were taken after acid addition, then after 5, 15 and 30 minutes and then every 30 minutes thereafter and then filtered. (See Sampling procedures and analytical procedures 6.2.5 and assays required in appendix 3). With every sample taken, the redox was measured, then the sample was filtered and a ferrous titration done on the solution (see attached procedure). The solids were reslurried and recharged to the autoclave with the required calculated amount of acid to maintain the required acid concentration. The solution samples were assayed for Cu, Ni, Fe, Se, Te, Ru, Rh, Pd, Pt and Au, with PGMs done only on the final samples. The dry solids were filtered after completion of leach and the dry mass measured.

Experimental procedure for sodium sulphite tests

The autoclave was filled with 7 litres of Na_2SO_3 (200g/l) solution. A solution sample is taken and a titration done for the concentration (See analytical assay procedure for sodium sulphate concentration analysis). Again the autoclave is purged with nitrogen while the agitator is started and the contents heated to the correct temperature. Once at the correct temperature, the oxygen is opened to the vessel and the pressure control valve fully opened for atmospheric conditions. A sample of the contents is taken every 15 minutes and a titration done to determine the conversion rate of sodium sulphite to sodium sulphate. The test continues until such time that good conversion data has been established.

6.2.5 Analytical procedures

In order to determine the sulphite concentration in solution, a back titration method with iodine was used, further titrating the iodine not converted with sodium thiosulphate. The method and calculations are shown in Appendix 3.

In order to determine the ferrous concentration in solution, the solution is titrated with potassium permanganate. The method and calculations is shown in Appendix 3.

In the solution samples, concentrations of copper, iron and nickel were determined by inductively coupled plasma (ICP) spectroscopy. Concentrations of selenium, tellurium, lead, and platinum group metals (PGM) including palladium, platinum, rhodium and ruthenium, will be determined by inductively coupled plasma-mass spectrometry (ICP MS).

Solid samples were dissolved by leaching in aqua regia and then analysed for cobalt, copper, iron and nickel content by ICP. Antimony, arsenic, bismuth, lead, selenium and tellurium were analysed by ICP MS.

6.2.6 Mineralogical methods

All the samples were air dried, after which representative splits were used in each case to prepare polished sections and X Ray diffractometric (XRD) scans. XRD is used to identify the composition of any crystalline phases present; results can be reported in a semi-quantitative fashion by implementing Rietveld analysis of the diffractograms.

All polished sections were examined by reflected light and scanning electron microscopy (SEM) techniques. Special care was taken to mount the agglomerated ‘balls’ sampled from some of the samples without breaking them up.

Bulk modal results, yielding mass percentage concentrations of the compositionally distinct species represented in the polished sections were obtained by the mineral liberation analysis (MLA) technique. 20 000 individual points per polished section were analysed to yield the data for the bulk modal analysis.

It should be noted that determination of elemental sulphur by scanning electron microscopy is problematic. Sulphur dissolves in the epoxy used to mount the powders and may also be vaporised by the electron beam under high vacuum at the voltages applied for analysis. Analytical results for selected elements were available for all the mineralogical samples. Analyses were performed in the Analytical Chemistry Department (Germiston Campus) at AR. Details of all the mineralogical techniques used during the investigation appear in Appendix I. Quality control of the mineralogical data involves a comparison of major element compositions determined chemically to corresponding data obtained by bulk SEM/XRF technique, by back-calculation of the bulk modal MLA and Rietveld (XRD)assay.

6.2.7 Calculations

Solids extraction calculations are based on the difference between initial element mass and final element mass, expressed as a function of initial element mass.

Solution extraction calculations are based on the difference between initial element mass and final element mass in solution, expressed as a function of initial element mass.

Calculation of sulphide sulphur and elemental S could be erroneous due to the fact that the portion of the base metals in NaOH residue was likely to be in hydroxide form and not in sulphide form. The sulphide sulphur is calculated from the copper, nickel, cobalt and iron in the NaOH residue, assuming that all of these elements are associated with one sulphur, ie CuS, NiS, CoS and FeS. This will give the total sulphide sulphur content. Based on mineralogy, the portion of hydroxide/ oxide species of these elements is approximately 20%, but the assumption was made that all of the copper, nickel and iron were present as monosulphides.

The final volume decreased during the leach, and this was taken into account and a correction made when calculating the solution extraction data.

In determining the amount of Fe precipitation during the leach, the amount of Fe added was taken into account.

All PGMs extractions were based on solution assay results.

6.3 Comparison between Different Residue Types – Results and Discussion

In the Introduction and Objectives and Materials and Methods sections, a comprehensive description is given of the origin and comparative results of the different residue types. The NaOH leach residue was produced from the CPL A residue, employing a continuous caustic leach, as was described in detail in section 5. The objective of testing the different residues, ie A and B with a direct sulphuric acid leach with A being treated with NaOH first, was to ensure that there really is a benefit in pre-treating the residue via a NaOH leach, before leaching with a pressure sulphuric acid leach. The different residues were tested under similar conditions, ie leaching at a temperature of 140°C, 340kPa pO_2, 2g/L Fe, 30g/L acid and 280 rpm agitation speed.

6.3.1 Mineralogy and general discussion

The mineralogy (table 26) of the three types of residues was analysed, and the major difference between the residues was the proportion of elemental sulphur. These residues were then leached using sulphuric acid as lixiaviant, and after 144 minutes of leaching, the mass loss from the B residue **(see Picture 3)** was only 9% and sulphur balls and agglomerates formed. It is clear from **Table 34** that there is no substantial mineralogical difference between the B residue before and after the leach (see also Appendix IV, **Pictures 11** and **12**). Also, the elemental sulphur present is of the orthorhombic type, ie it has a structure that indicates it originated from molten elemental sulphur. The material contained in the agglomeration **(Picture 3)**, does not differ mineralogically from the initial residue B. It is merely encapsulated in a layer of elemental sulphur. It should be borne in mind that, following the planned BMR upgrade, this would be the likely form of residue produced if no further polishing was done.

The A residue did leach to some degree, but rapidly formed sulphur balls during the leach **(see Picture 4)**. Compared to residue B, it had a lot less elemental S initially, but formed more elemental S during the sulphuric acid pressure leach, which eventually began to inhibit the extraction of base metals. The mass loss on this residue was 52%.

Species	***Residue B***	***Residue B after H_2SO_4 leach***	***Residue A***	***Residue A after H_2SO_4 leach***	***Residue A after NaOH leach***	***NaOH residue after H_2SO_4***
	% Mass					
Covelite (CuS)	57	58	79	66	74	62
Chalcanthite ($CuSO4.5H_2O$)	0.12	0.16	0.2	0.3	2.6	0.7
Tenorite (CuO)	0	0	0	0	16	0
Alt Bornite(close to Cu_3FeS_4)	4.5	5.2	7.1	10	3.3	3.9
Fletcherite($CuNi_2S_4$)	0.1	0.5	3.4	2.1	3.9	1.6
Sulphur(S^o) Orthorombic	35	35	10	16	0	11
Sulphur(S^o) Amorphous	0	0	0	0	0	12
Refractory	1.7	0.1	0.4	0.5	0.7	0.9

Table 34: Comparison between residues before and after H_2SO_4 leach

In appendix IV, **Pictures 13 and 14**, the MLA maps of residue A before and after the leach are shown, and the concentration of covelite is a lot higher in the ‘before’ than in the ‘after’ maps. Also, the sulphur present is of the orthorhombic type, ie it has a structure that indicates it originated from molten elemental sulphur. The material contained within in the sulphur balls **(Picture 4)**, does not differ mineralogically from the initial residue A – it is merely encapsulated in a layer of elemental sulphur.

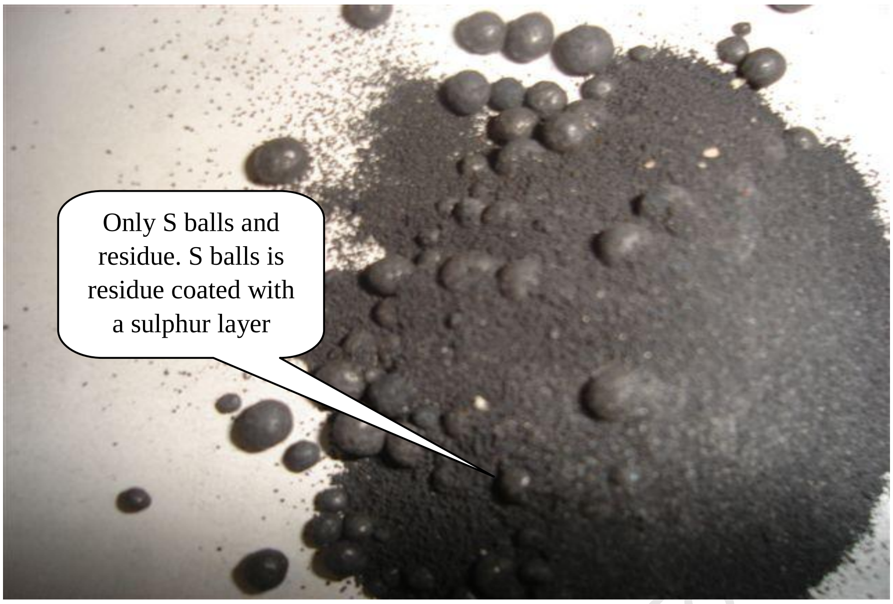
No sulphur balls were noticed when the caustic leach residue, as produced in section 5, was leached under the same conditions in sulphuric acid **(see Picture 5)**, although some elemental S did form during the sulphuric acid leach. This material had the biggest mass loss (64%) after leaching, even considering that the leach was 20 minutes shorter than that of the A residue. This indicates that the NaOH leach residue leached better under the same conditions as the A residue, but it must be borne in mind that 9% of elemental S contained in the A residue was removed and therefore not present in the NaOH residue, and that the elements in the NaOH residue were more concentrated by comparison. (See table 33). The material was also a finer grained residue than residue A after the sulphuric acid leach, which was not really evident in the residues before the leach started. There was no elemental S present at the start, so this is possibly the difference. In Appendix IV, **Pictures 15** and **16**, show the MLA maps of the NaOH residue before and after the leach. In the A and B residues all the elemental sulphur was present as orthorhombic sulphur, but now the appearance of amorphous sulphur was noticed in the NaOH residue after the acid leach. The difference in the two types of sulphur, as indicated by the mineralogy department, is possibly:

(i) Orthorhombic S is elemental sulphur which retains its structure even when molten and cooled again.

(ii) Amorphous S does not have a structure. At this stage further work needs to be done in order to better define this type.

As can be seen from **Table 33**, there is a more even distribution between orthorhombic and amorphous sulphur in the NaOH residue after sulphuric acid leach.

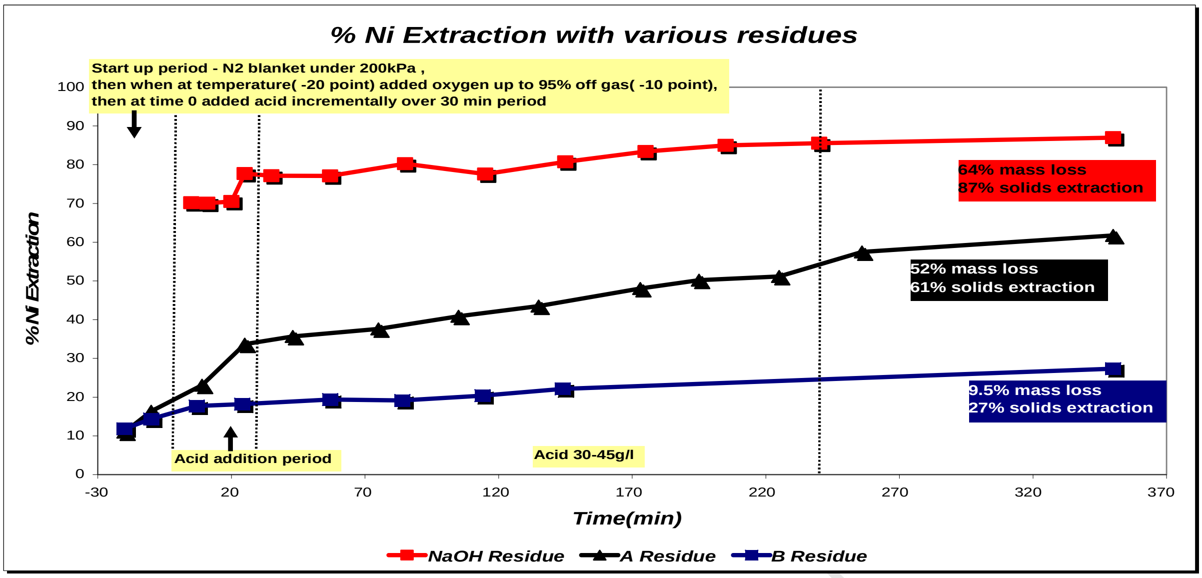
Picture 3: B residue after H2SO4 leach



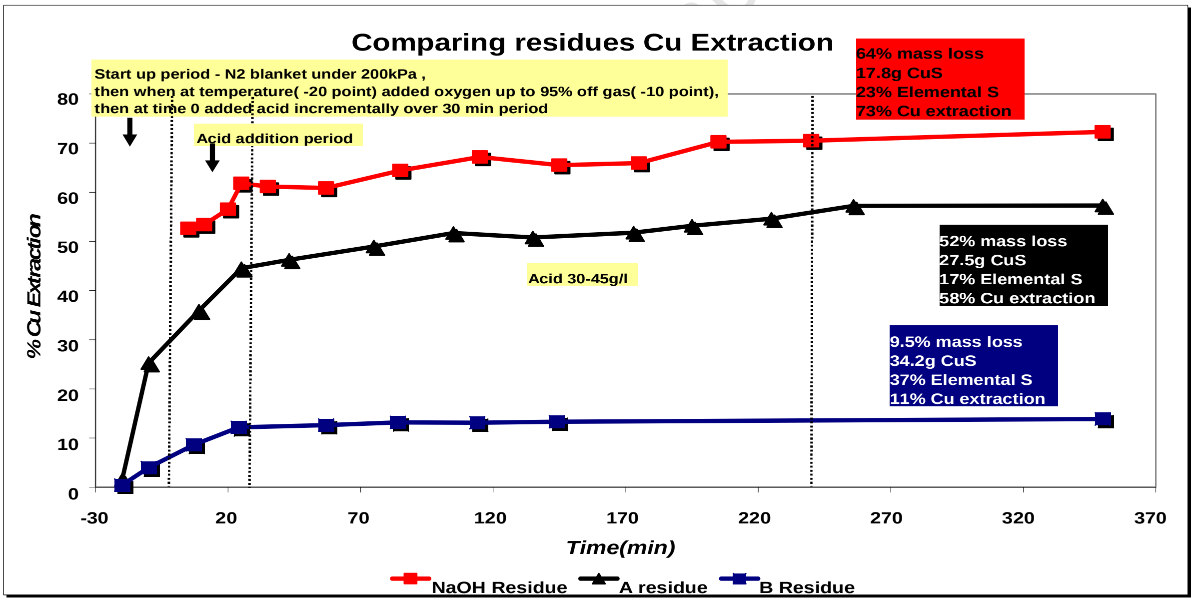
Picture 4: A residue after H2SO4 leach

Picture 5: NaOH residue after H2SO4 leach

6.3.2 *Base metals (Cu, Ni, Fe and S)*



Graph 28: Ni extraction from solution assays – comparing different residues



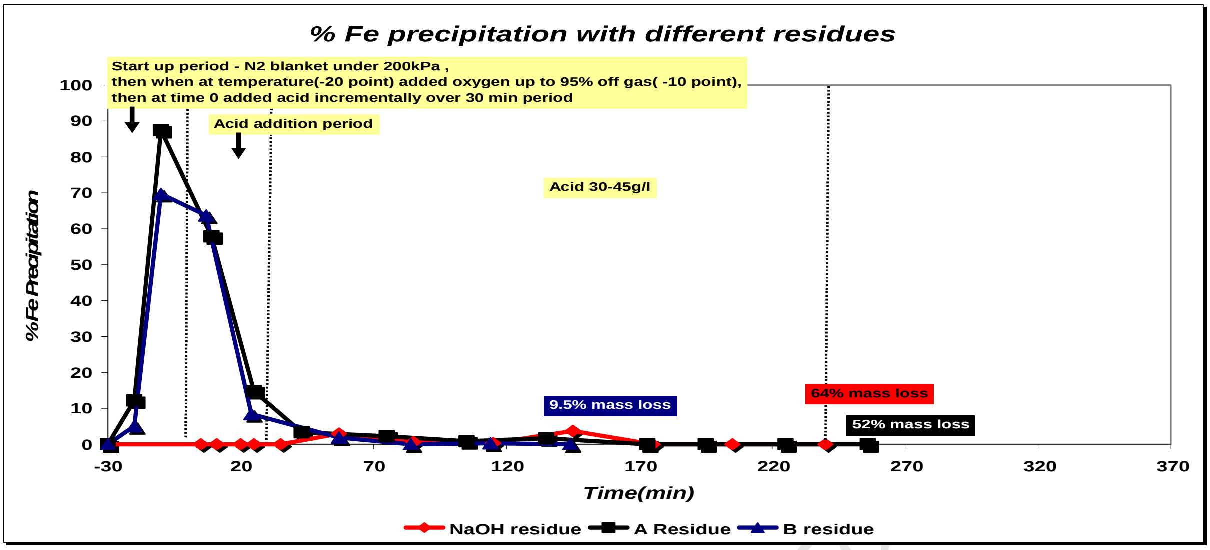
Graph 29: Cu extraction from solution assays – comparing different residues

During the heat up period (about 25 minutes), with the autoclave under nitrogen pressure, the ferrous concentration in solution drops from 2g/l to 1.6g/l due to ferrous precipitation (assumed pH ±7, demin. water), and the ferrous ions have precipitated to between 5–12 % of the sum of the Fe present in the residue and the ferrous added to the solution **(see Graphs 30 and 31)**. This precipitation is due to the lack of acid present. At this stage Ni has leached 12% and Cu 1.5%, with just the small amount of the acid generated from the ferrous precipitation **(see Graphs 28 and 29)**.

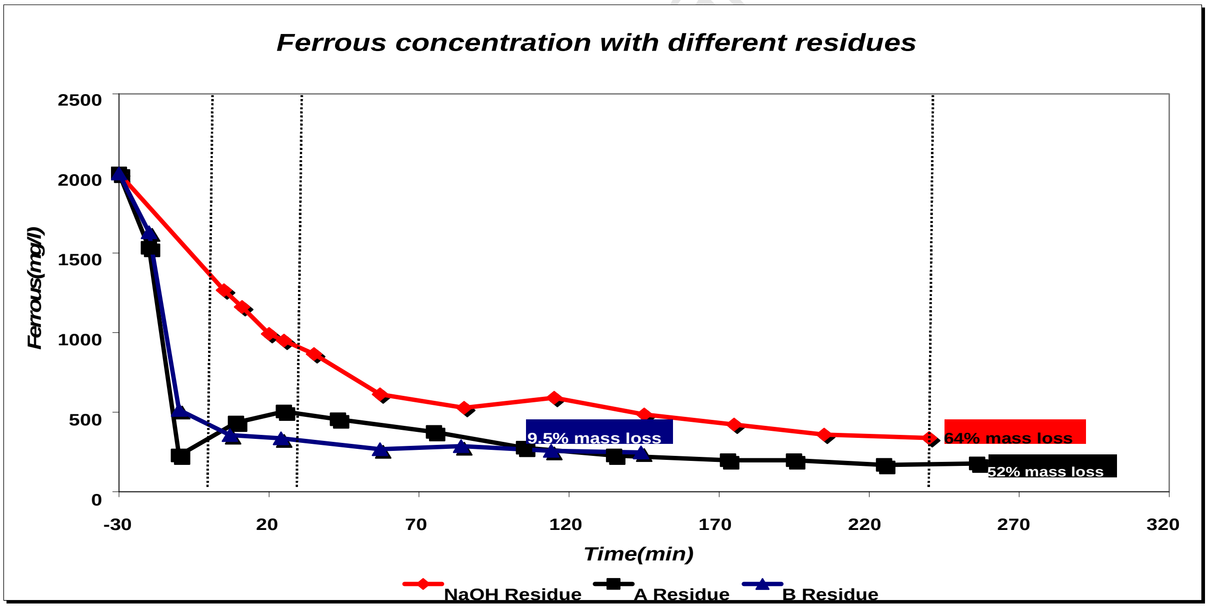
After this, oxygen is added to the reactor and allowed to stabilise to 95% O_2 in the off gas (about 5 minutes). During this period the ferrous concentration decreased dramatically to between 200–500ppm in solution, simply because most of the Fe was precipitated and very little was left in the solution phase. Oxygen probably oxidised the remainder of the ferrous in solution to ferric ions, which subsequently precipitated (70–88% of all Fe added to the mix), generating acid. The combined action of the ferric ions (at any stage less than 500ppm) and the oxygen contributed to the oxidation/ leaching of Ni (15%) and Cu (25%) within 5 minutes. The ratio of the ferric to the ferrous concentrations in solution is extremely low at this stage, resulting in a redox potential between 370–400mV (Ag/AgCl).

Once the acid addition stage commences, Fe starts to redissolve within 7 minutes **(see Graph 30)**, and the redox increased to 450mV **(see Graph 33)**. The Ni extraction increases to 23% and copper extraction to 35%, over a period of about 12 minutes in residue A. The NaOH residue at this stage has dissolved and oxidised to 53% Cu in solution. This indicates that 18% is due to dissolution of hydroxide species and around 35% due to the combined oxidation potential of the ferric and oxygen. By the end of the acid addition period (25 minutes), most of the Fe has redissolved and the ferrous concentration is between 500–1 000 ppm in solution, the ferric to ferrous ratio is about 1.5 to 3, and the redox potential has jumped to 470–490 mV (Ag/AgCl). The copper extraction at this stage has increased to 62% in the NaOH leach residue and 45% in the A residue. Ni extraction increased to 78% in the NaOH residue and 34% in the A residue.

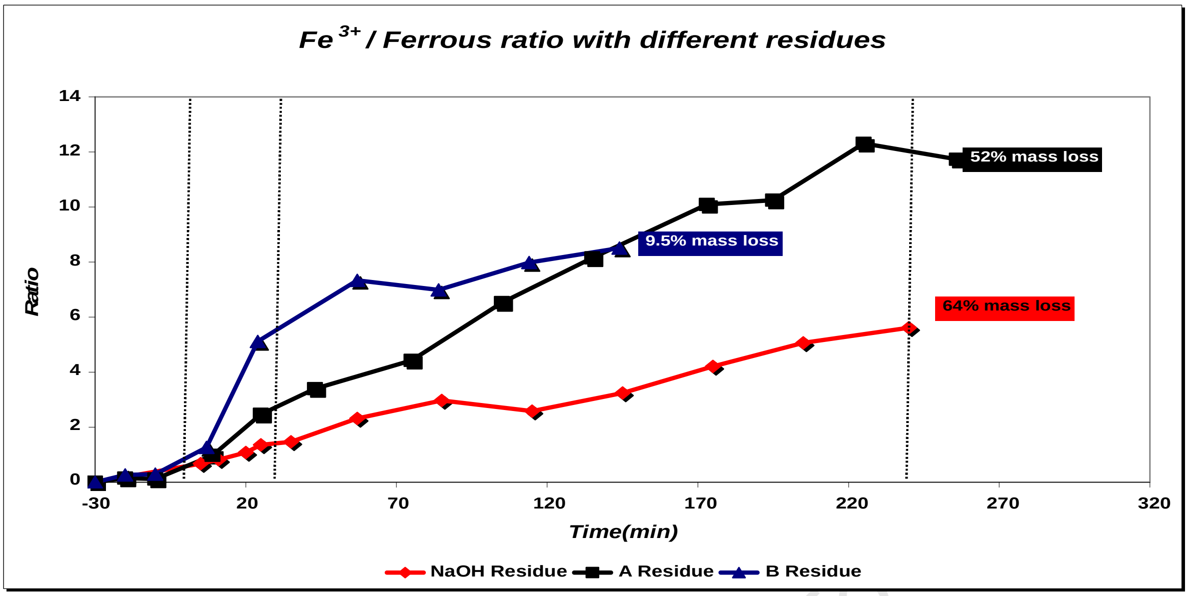
After this acid addition period, the extraction rate of Cu and Ni decreased enormously due to the formation and melting of elemental S. Cu extraction only increases by 10% in the next 210 minutes. This is significant, because it would then appear as if most of the oxidation work is done (80% of the Cu is oxidised) within the first 30 minutes of leaching time, and the remaining 20% oxidation occurs over another 3.5 hours. The total Fe in solution converts to ferric a lot quicker (B residue> A residue> NaOH residue) **(see Graph 32)**, and the redox potentials measured are indicating this same trend – the reason being that a large proportion of the material is trapped within a sulphur capsule, and the oxidant cannot reach the sulphide minerals.



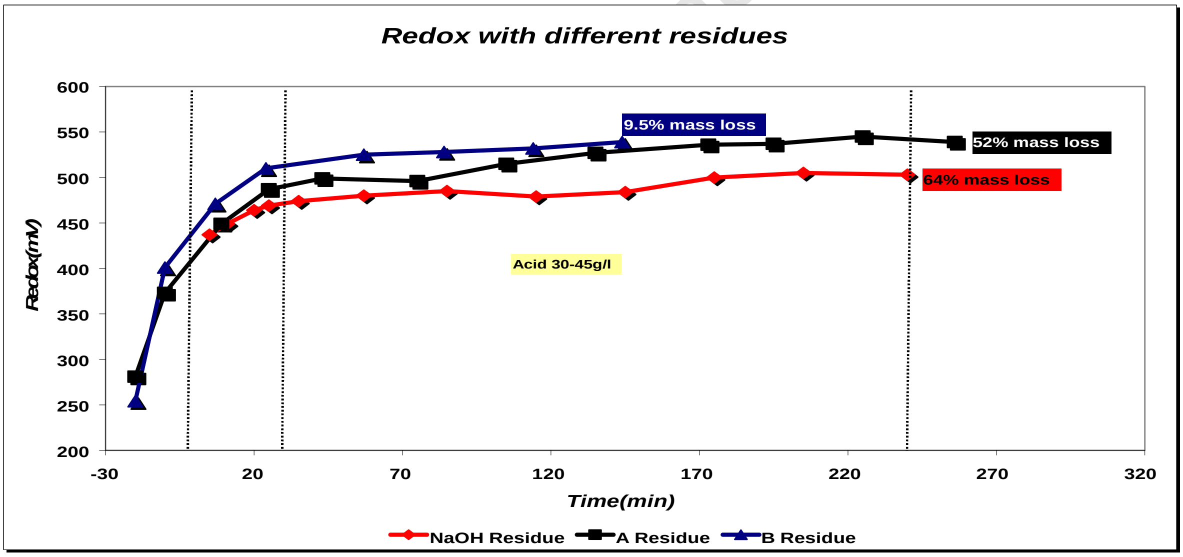
Graph 30: Fe precipitation – comparing different residues



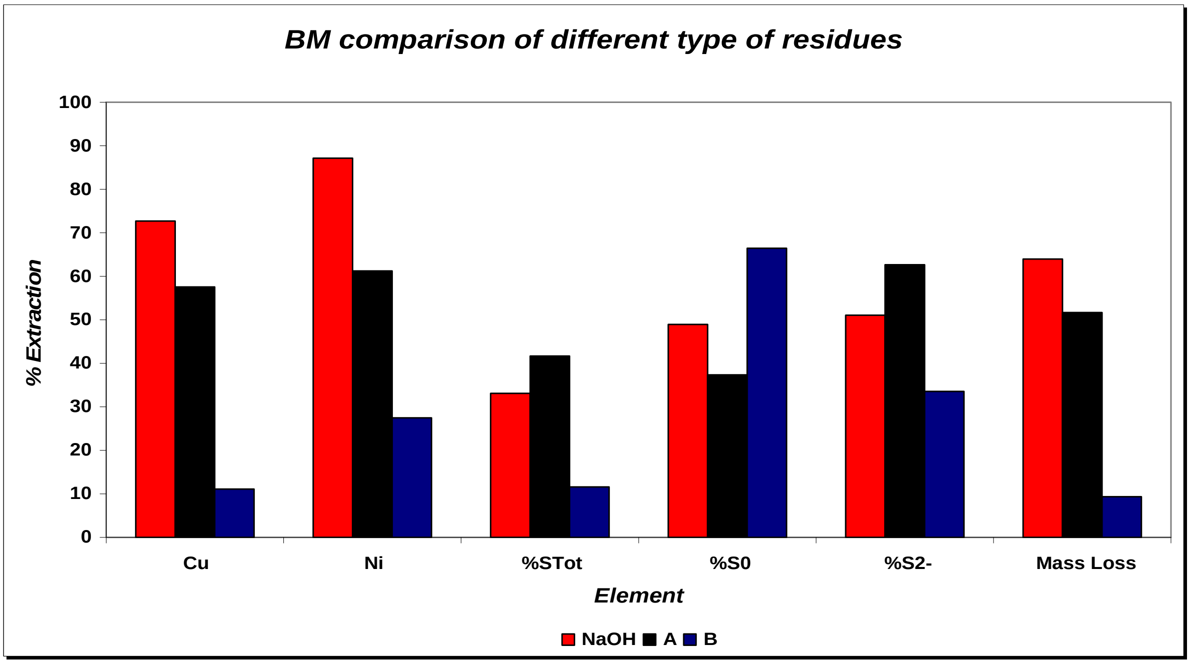
Graph 31: Ferrous concentration – comparing different residues



Graph 32: Ferric to ferrous ratio – Comparing different residues



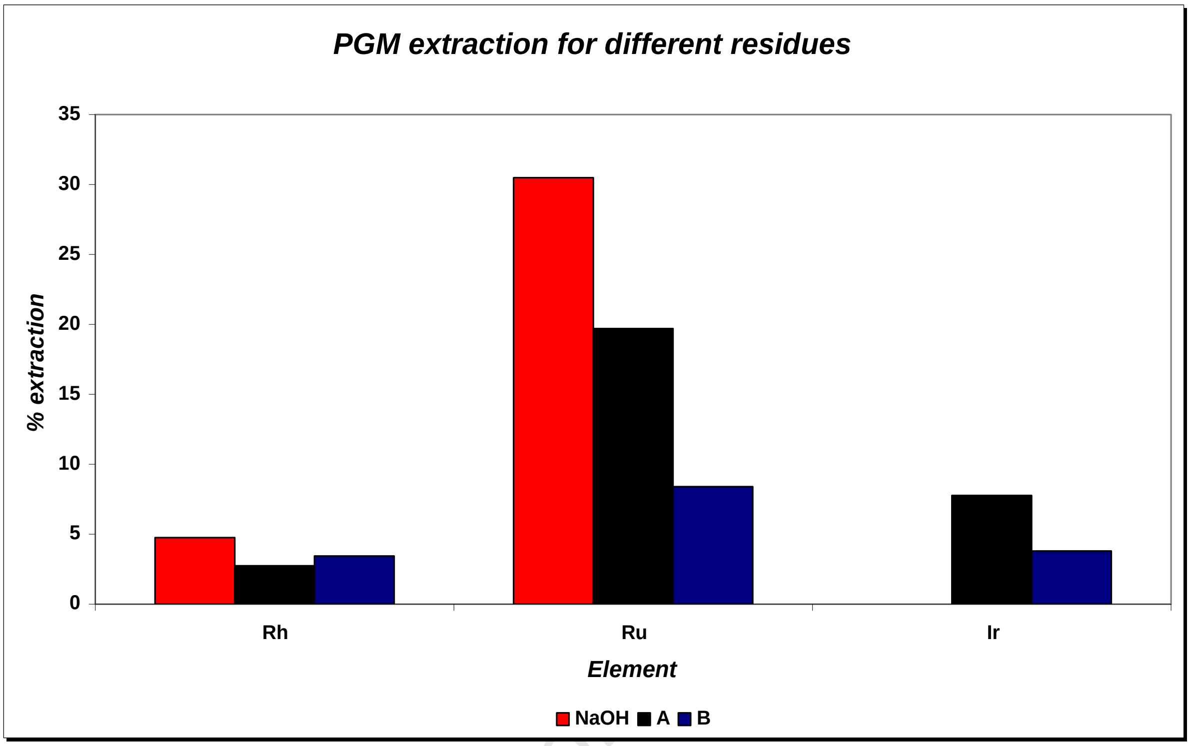
Graph 33: Redox – Comparing different residues



Graph 34: Base Metal extractions calculated from solid assays – Comparing different residues

Copper and nickel extractions differ widely between the different residue types, clearly demonstrating the need for the NaOH leach and the difference it makes in extraction of these elements. Total sulphur extraction, however, did not follow the same trend as it did for the base metals. Even though there is a much higher degree of base metal extraction in the NaOH residue than in residue A, there is a higher sulphur extraction in residue A. The reason for this is the amount of elemental S present in residue A being oxidised preferentially over the base metals. Potentially, with an elemental S coating around the particles, more oxidant will be used for its oxidation before it can get to the particle surface where it can leach sulphide minerals. Furthermore, this molten elemental sulphur tends to stick together and agglomerate, occluding a portion of the residue, effectively isolating it from the oxidant **(see Graph 34)**.

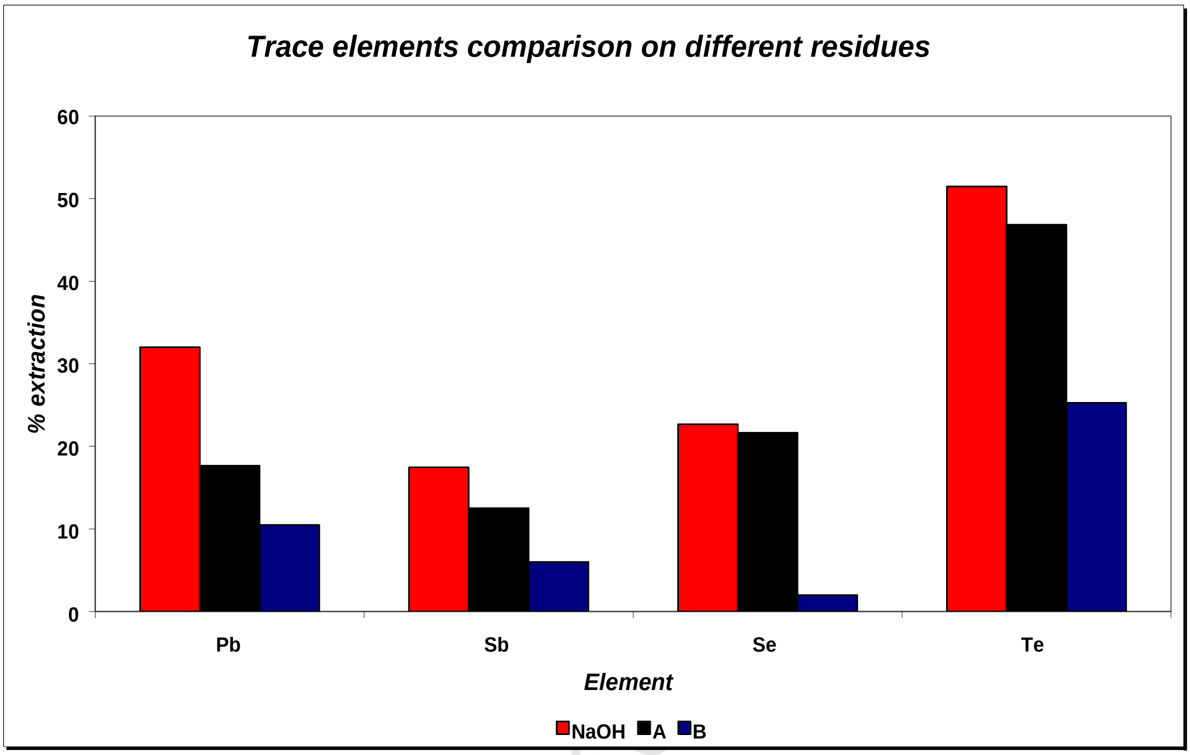
6.3.3 PGMs



Graph 35: PGM extractions calculated from solution assays – Comparing different residues

Slight differences exist in rhodium and ruthenium extractions from the 3 residues, but these trends are similar to those of the base metal extractions **(see Graph 35)**. The final PGM extractions are relatively high based on solution assays, but negligible based on solid assays. Given the low concentrations measured, all results relating to PGM extractions must be treated with some caution.

6.3.4 *Trace elements*



Graph 36: Pb and Sb calculated from solution assays, Se and Te from solid assays

Also for the trace element extractions, the same trends are followed as those observed for base metal extractions. Selenium extraction calculated from solids assays is in the order of 20%, while Tellurium is 40–50 %**(see Graph 36)**.

6.4 General Observations and Results of Ferrous Variations

In order to test the influence of ferrous addition on the leaching of the NaOH residue, four tests were done under the same conditions, only varying the ferrous ion addition. It must be noted that in all the test work done from hereon, the only residue used was the NaOH residue.

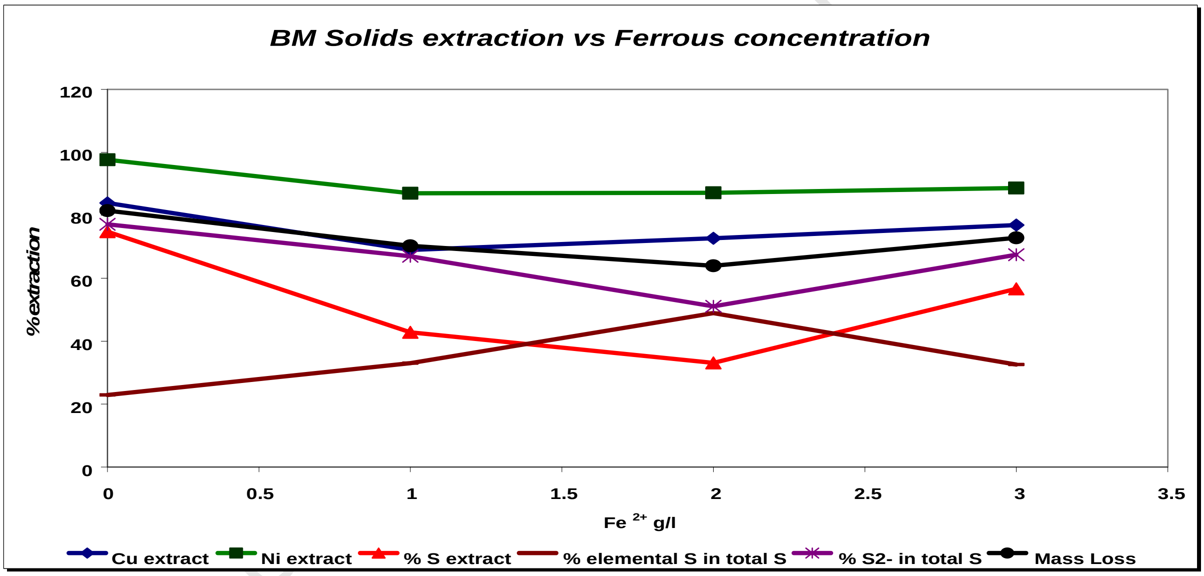
Conditions

Temp : 140°C
pO2 : 340kPa
Agitation rate : 280rpm
Acid : 30g/l
Fe addition : 0, 1, 2 & 3g/l

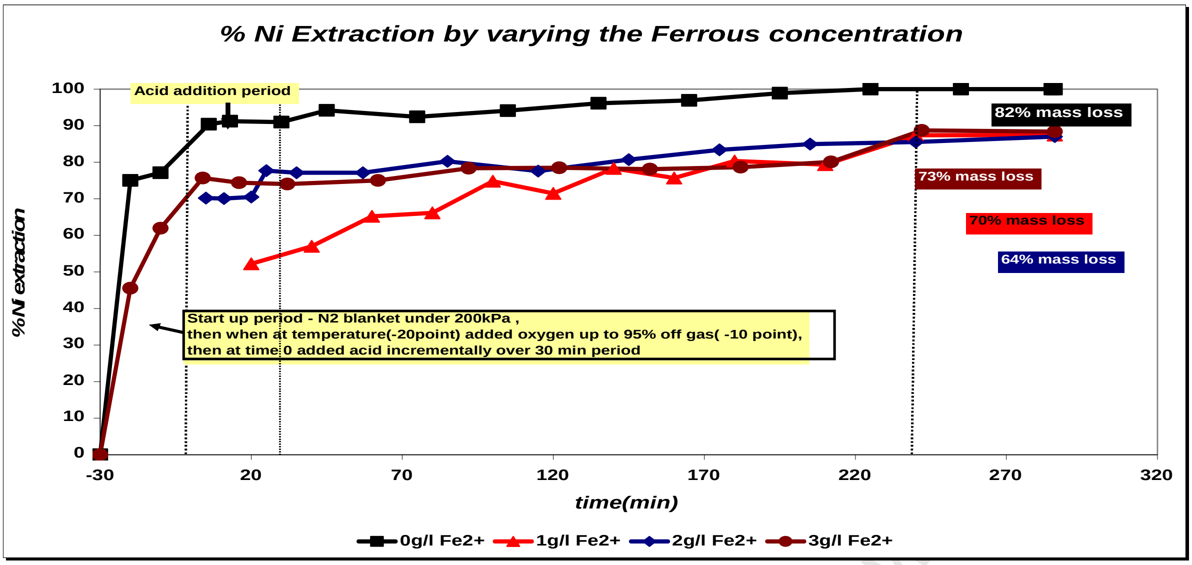
Leach times	:	240 minutes for 1, 2 & 3g/l Fe 285 minutes for 0 g/l Fe

6.4.1 Base metals (Cu, Ni, Fe and S)

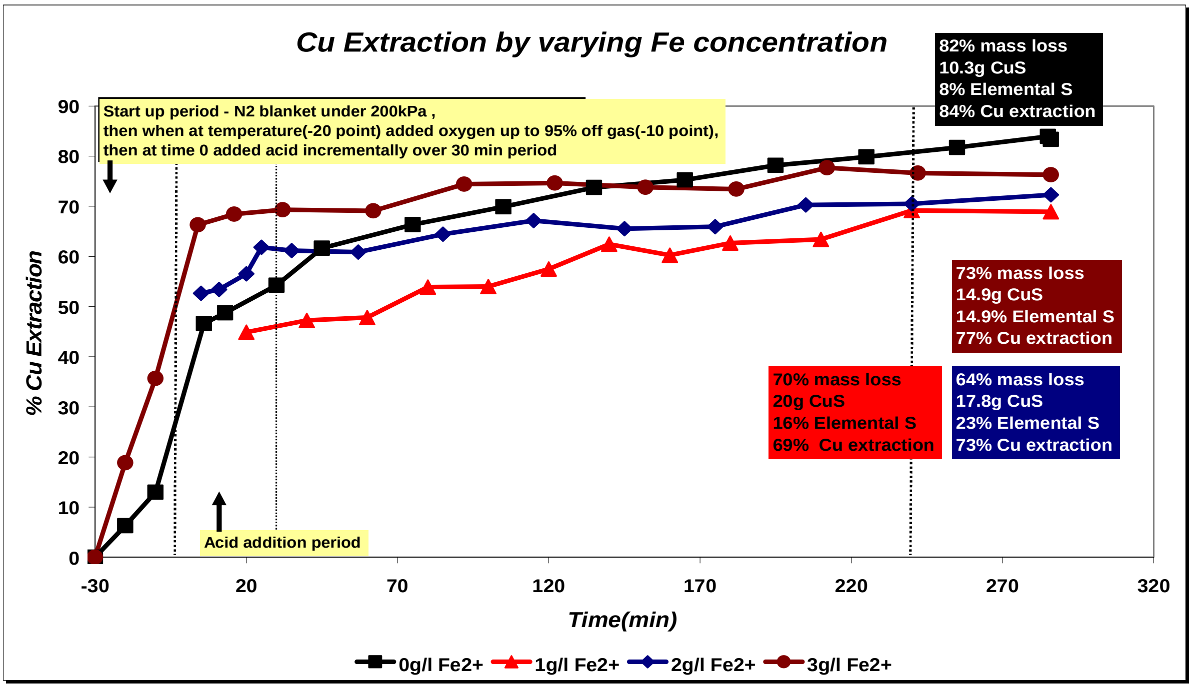
At 0 g/l ferrous addition, the filtered solutions had a bluish colour instead of the otherwise typical greenish colour. No sulphur balls were observed in the residues under any of the conditions. The highest mass loss was obtained when no ferrous was added to the leach, but this leach was run for 45 minutes longer than the others. Samples were taken after the initial warm up period (25 minutes) and after the oxygen addition period (5 minutes) only during the 0g/l & 3g/l ferrous addition tests. Unfortunately, no samples were taken in the other two ferrous variations during these periods.



Graph 37: Base Metal extractions based on solids assays – Varying ferrous concentrations



Graph 38: Ni Extraction based on solution assays – varying ferrous concentration



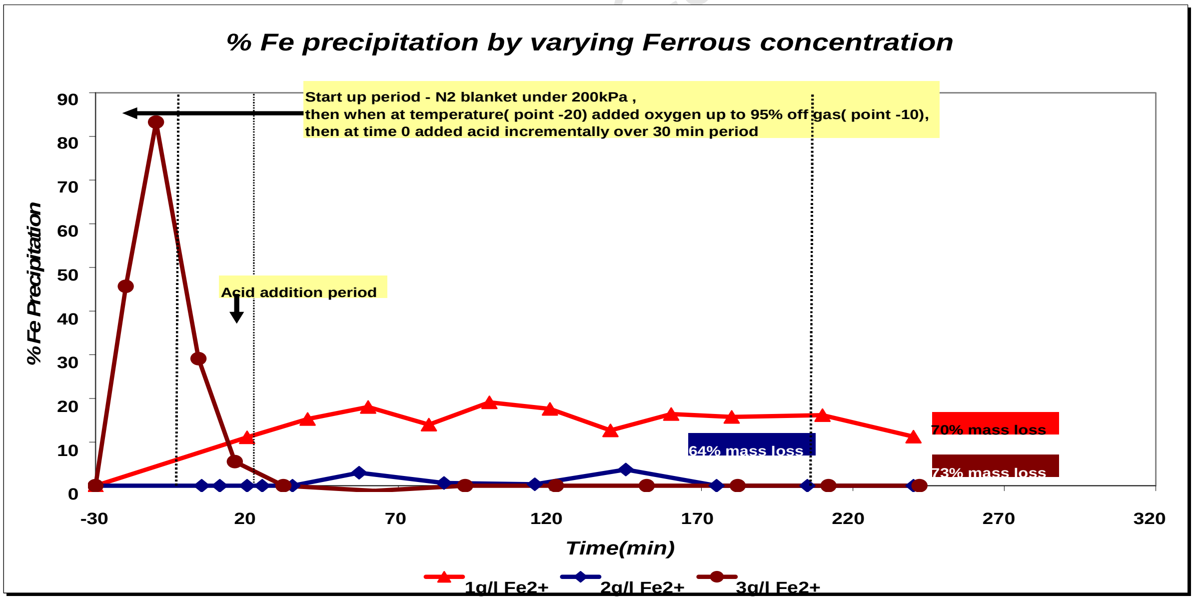
Graph 39: Cu extractions based on solution assays – Varying ferrous concentration

During the heat up period (about 25 minutes), with the autoclave under nitrogen pressure, the ferrous concentration in solution drops **(Graph 41, 3g/l Fe test)** due to precipitation, and the ferrous ions precipitated to 45 %. At this stage Ni has leached to 75% at 0g/l Fe, 45%, at 3g/l Fe and Cu to 6% at 0g/l Fe and 19% at 3g/l Fe, apparently just with the small amount of the acid generated from the ferrous precipitation **(Graph 38 and 39)**. The Ni and Cu extractions in the other two variations of ferrous addition are assumed to be somewhere between the high and low scenario. But significantly, as no Fe is present in the 0g/l test, it could not have precipitated and generated acid. Since there is no oxygen at this stage either and only 87 ppm ferrous in solution (possibly background concentration), there cannot be any ferric ions at meaningful concentrations. It needs to be asked, therefore, by what mechanism Ni has been extracted to such a large extent. Although perhaps not very significant, 6% of Cu has also been extracted at this stage. This will be discussed in detail in section 6.9.2.

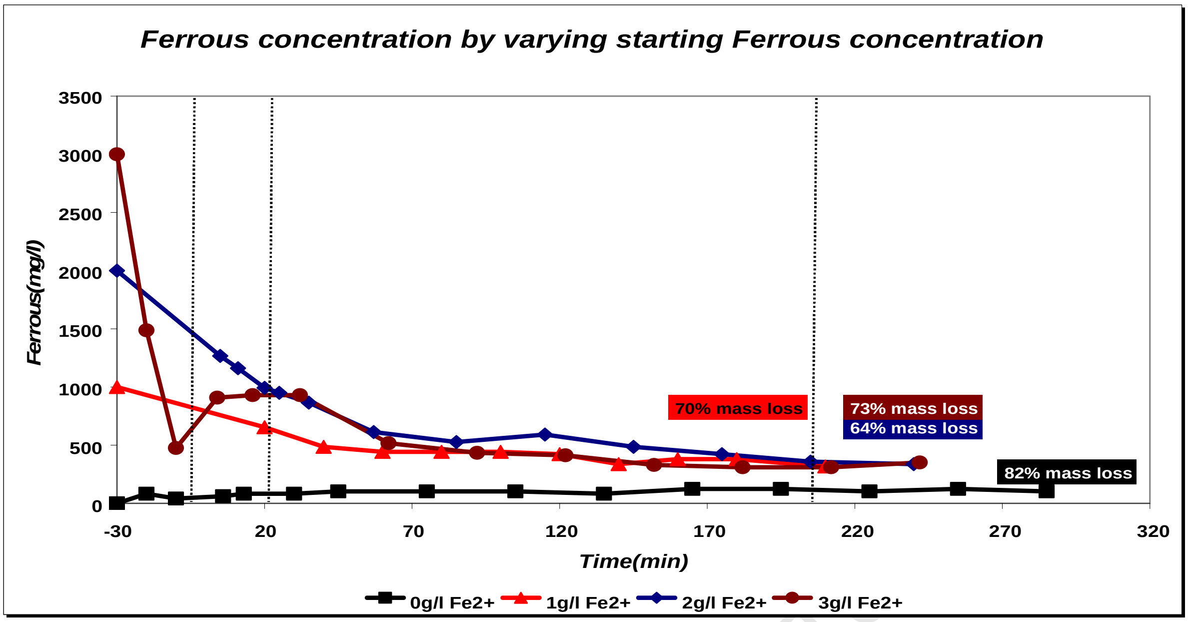
After the initial oxygen addition period (ca. 5 minutes), the ferrous concentration decreases dramatically to 475 ppm **(Graph 41)** in solution (3g/l Fe addition), simply because most of the Fe was oxidised to ferric and mostly precipitated (83%) **(Graph 40)**, generating acid. The combined action of the ferric ions, at most between 0–500 ppm, and the oxygen then oxidised Ni (62%) and Cu (35%) in the 3g/l ferrous addition test within 5 minutes. In the 0g/l ferrous addition test, Ni extraction was at 77% and Cu extraction at 13%, respectively. However, as was stated above, most of this had already been in solution by the time the oxygen was switched on. It also appears as if the addition of ferrous ions to the mix has very little to do with the oxidation of Ni, but it has a marked impact on the initial Cu extraction. When comparing the residue runs (A residue), with the Fe addition runs (NaOH residue) in 6.3.2, Cu extraction has increased by at least 10% during this short period, which is possibly directly related to the extra addition of ferrous ions to the mix. The ratio of the ferric to ferrous ions in solution is extremely low at this stage **(Graph 42)** with redox potential measuring between 320–350mV Ag/AgCl **(Graph 43)**.

As the acid addition stage commences, the ferrous ion concentration started increasing within 7 minutes, and the redox potential increased to 475 mV Ag/AgCl in the 3g/l test and 414 mV in the 0g/l Fe test. The Ni extraction reached 76% and copper extraction 66% within about 12 minutes in the 3g/l ferrous test. In the 0g/l ferrous test Ni extraction was at an even more significant 90%, with Cu extraction still at 47%. This possibly indicates that 20% is due to hydroxide dissolving and possibly 46% due to the combined oxidation potential of the ferric and oxygen. By the end of the acid addition period (25 minutes), most of the Fe has redissolved and the ferrous concentration is between 500–1 000 ppm in solution, the ferric: ferrous ratio is between 0 – 2.4 and the redox has increased further to 500 mV (Ag/AgCl) in the 3g/l Fe run, but remained at 400mV (0g/l Fe). The copper extraction at this stage has increased to 70% in the 3g/l ferrous test and 55% in the 0g/l test, and Ni extraction to 74% in the 3g/l ferrous test and 91% in the 0g/l ferrous test. After this acid addition period, the extraction rate on Cu virtually stopped, presumably due to the formation of elemental S in the case where ferrous was added to the leach, but another 30% Cu extracted where no ferrous was added. This is significant, because it would then appear as if most of the oxidation work in terms of Cu is done within 30 minutes leaching time in the cases where ferrous ions had been added to the leach. The remaining 3.5 hours of leaching were basically wasted on oxidising elemental S to sulphate, but little else.

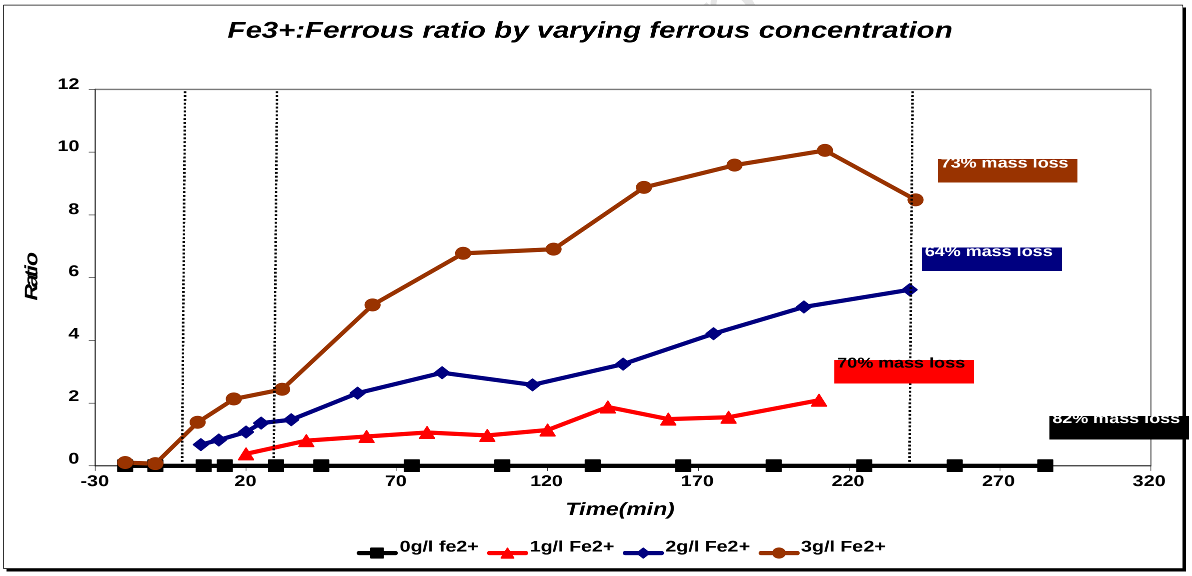
With reference to **Graph 39**, after 4 hours of leaching, the Cu extractions were higher with higher initial ferrous ion concentrations, if just comparing the tests where some Fe was added to the leach. But when no additional ferrous ions were in the mix, final Cu extraction was the highest, even though the initial extraction rate of Cu was not that fast.



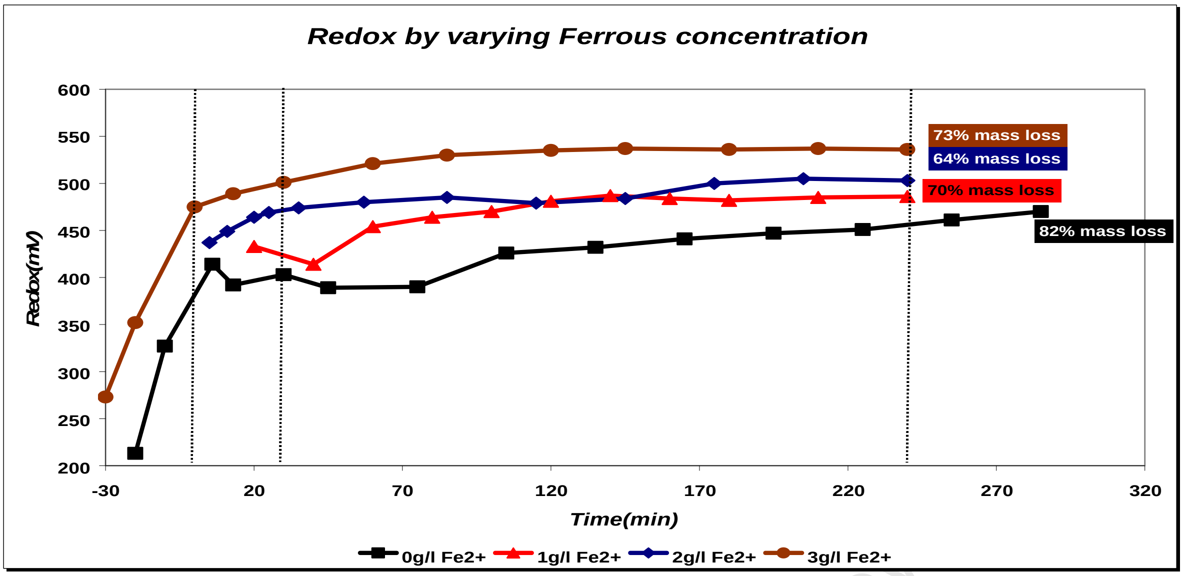
Graph 40: Fe precipitation by varying ferrous concentration based on solution assays



Graph 41: Varying initial ferrous concentration

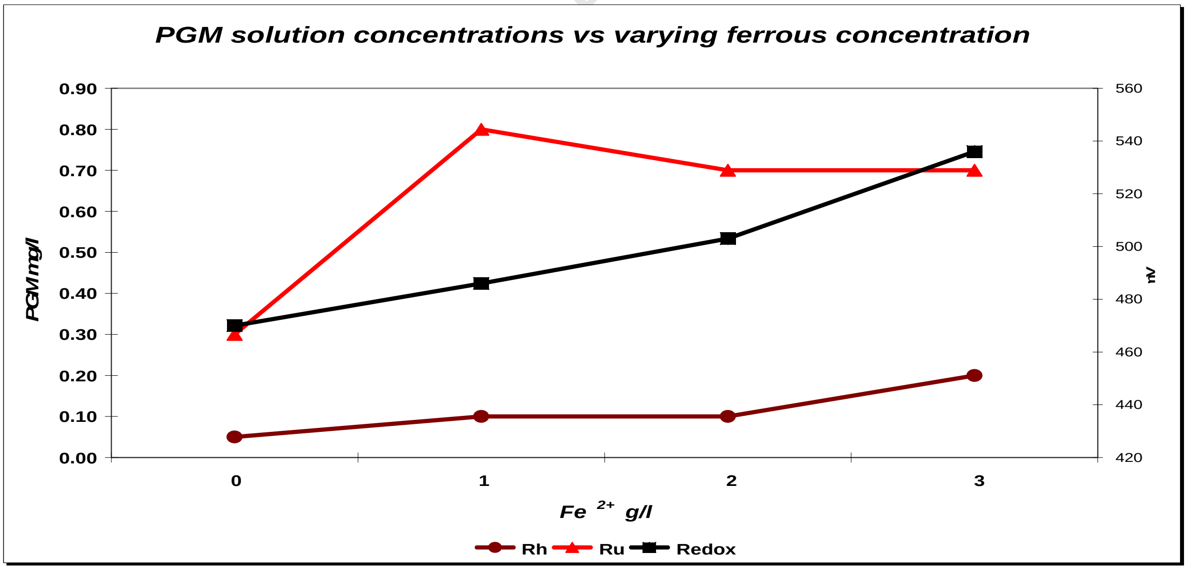


Graph 42: Ferric to ferrous ratio – varying initial ferrous concentrations



Graph 43: Redox by varying initial ferrous concentration

6.4.2 PGMs

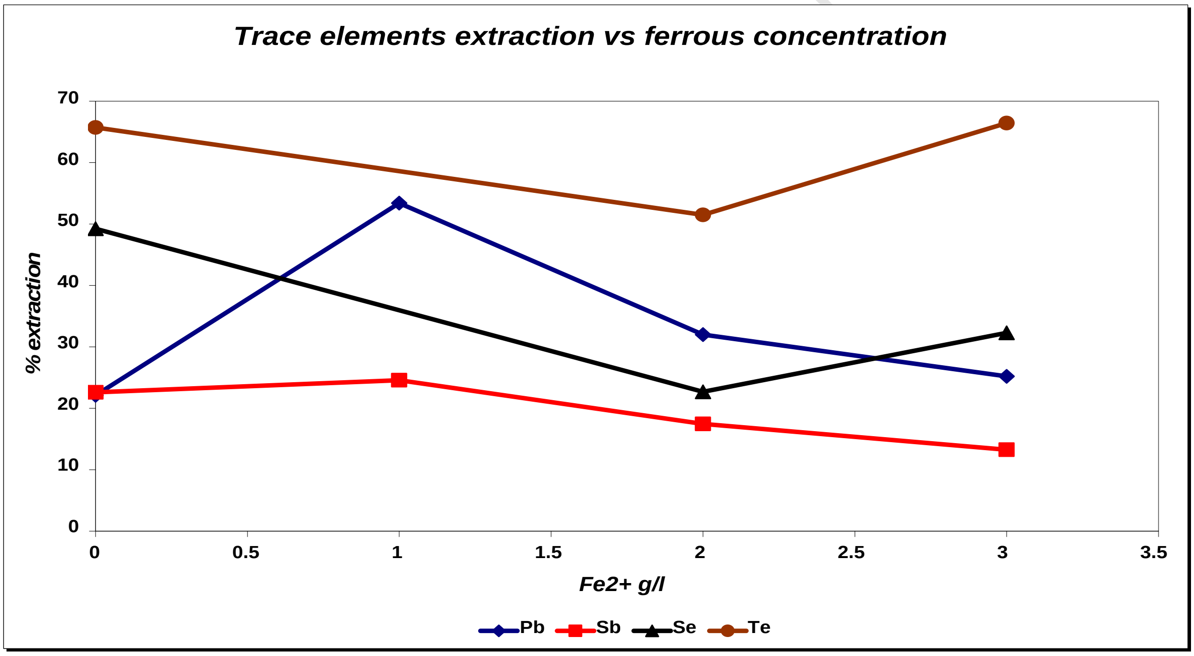


Graph 44: PGM concentrations by varying initial ferrous concentration

It appears by increasing ferrous ion addition that the Rhodium extraction also increases, and the difference between 0 g/l ferrous and 3g/l ferrous addition, rhodium extraction increases 4 fold. This is possibly due to the substantial increase in redox potential which accelerates all the reactions. It must also be taken into account that the test done at 0g/l ferrous addition was

45 minutes longer. Ruthenium extraction also doubles as soon as any ferrous ions are added to the leach. As the oxidation potential increases, Ru (360mV) > Rh (490mV)>Pd (540mV)>Pt dissolution occurs. The relationship between ruthenium and rhodium solubility, and the total ferric concentration of a leach terminated in the potential range of 480–515mV at 140°C and 490–525mV at 150°C was described by Hofirek [21 & 22 & 28]. An increase in the solubility of both metals with increasing Fe concentration is apparent. It is well known that Fe precipitating acts as a good collector for soluble PGMs[21]. However, the analytical results reported were low (< 1 ppm), and to draw firm conclusions from this data is probably risky.

6.4.3 Trace elements



Graph 45: Pb and Sb extraction from solution assays, Se and Te from solids assays

When no Fe was added, the extraction of Se and Te is the highest. It appears as if some Pb and Sb extraction also occurs. The extractions calculated, especially for lead are very high, and, if true, must be remnants from the NaOH leach where the PbS mineralogy might have been altered.

6.5 Mineralogy, General Observations and Results of Temperature Variation

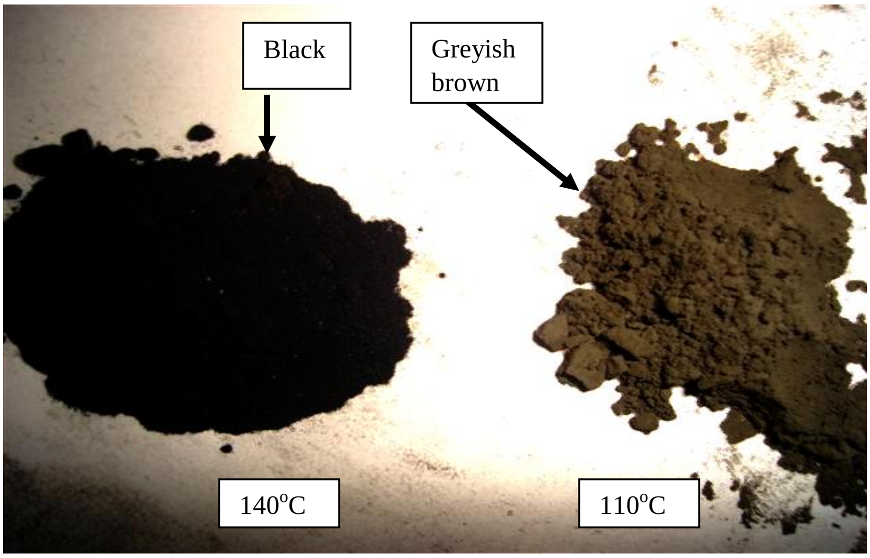
In order to test the influence of temperature on the NaOH leach residue, four tests were done under identical conditions, only varying temperature:

Temp : 110^{o}C, 130^{o}C, 140^{o}C, 150^{o}C
pO2 : 340kPa
Agitation rate : 280 rpm
Acid : 30g/l
Fe addition : 2g/l
Leach times : 110^{o}C and 130^{o}C 300 minutes
140^{o}C and 150^{o}C 240 minutes

During the temperature variation tests, unfortunately no samples were taken after the heat up period and after oxygen was opened to the vessel. However, the start up regime did not differ much from the previous tests.

No sulphur balls were observed in any of the residues in these four tests. **Picture 6**, illustrates the general colour and texture of the residues of the tests performed above and below the sulphur melting point. The highest mass loss was on the two low temperature leaches, (**see Table 38**), but these leaches were done for 300 minutes, 50 minutes longer than those at two higher temperatures. The copper extractions during these leaches were also the highest. There is a noticeable difference in the type of residue being formed during the lowest temperature (110^{o}C) leach and that at the other temperatures, which will be shown in the mineralogical analysis described below.

The mineralogy of the residues of two of the temperature tests (110^{o}C and 140^{o}C) were analysed, and there were major differences as can be seen in **Table 35**. Although the mass loss of the 110^{o}C test was 12 % more than the test done at 140^{o}C (**see Table 38)**, the residual covelite concentration in the 110^{o}C residue is 44% lower than for the test done at 140^{o}C. The sulphur in the two residues also differed substantially. The total elemental sulphur in the residue in the 110^{o}C test was 59%, while in the test at 140^{o}C there was 23% elemental S.



Picture 6: Showing colour and texture difference between 2 temperature variations

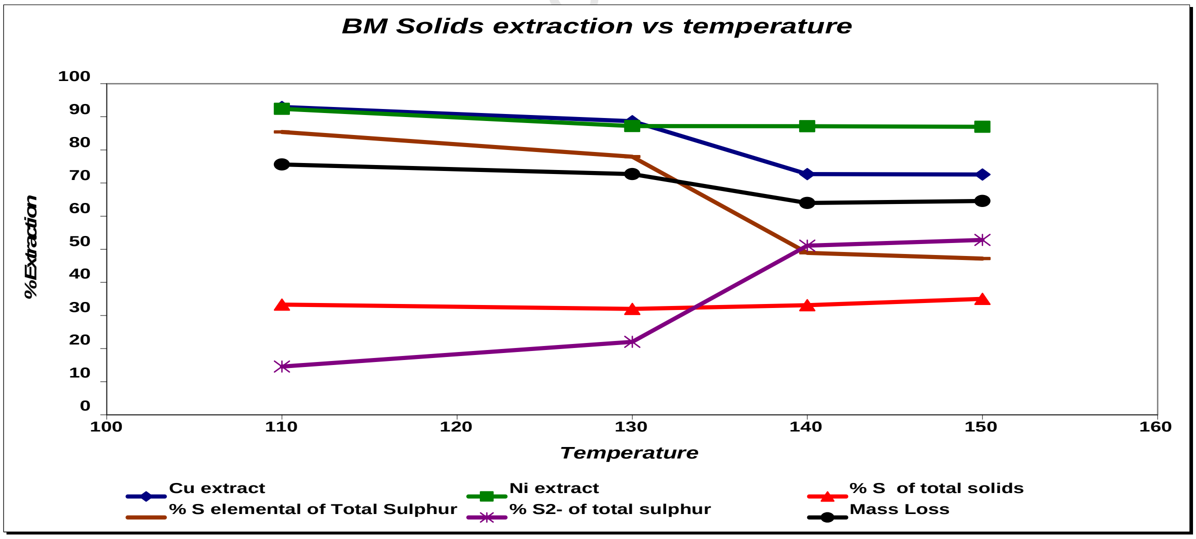
The types of elemental S which were formed in the low temperature test were 58% orthorhombic and 42% amorphous (See explanation in 6.3.1 Mineralogy and General discussion), while the test at 140°C is 48% orthorhombic and 52% amorphous. The starting residue, i.e. NaOH residue, had no elemental sulphur present. It is clear from the mineralogy, even though there were very good Cu extraction on the low temperature leach, very little sulphur oxidation took place. From actual analytical data the BM: S ratio is 0.13 in the 110°C compared to the 0.5 ratio at 140°C (see table 38). It is also clear from mineralogy that a lot of refractory material (mostly silicates which will not leach) appears in the low temperature leach which cannot be explained.

From the MLA maps in Appendix IV, Pictures 17 and 18, it is apparent that much more copper with much larger grain size is present in the higher temperature leach. This could indicate that some sulphur agglomeration did occur, but only visible under the instrument.

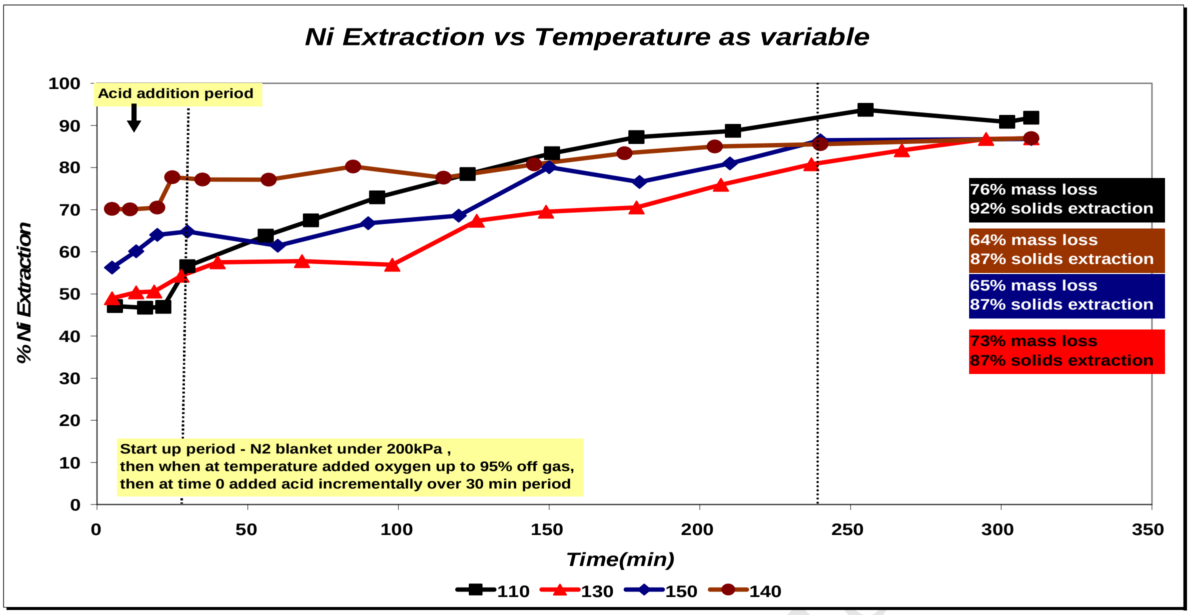
Species	***Residue A after NaOH leach Initial residue***	***NaOH leach residue after Temp at 140°C H_2SO_4 leach***	***NaOH leach residue after Temp at 110°C H_2SO_4 leach***
	% Mass		
Covelite (CuS)	74	62	18
Chalcanthite ($CuSO4.5H_2O$)	2.6	0.7	0.1
Tenorite (CuO)	16	0	0
Alt Bornite(close to Cu_3FeS_4)	3.3	3.9	2.3
Fletcherite($CuNi_2S_4$)	3.9	1.6	0.6
Sulphur(S^o) Orthorombic	0	11	45
Sulphur(S^o) Amorphous	0	12	32
Refractory	0.7	0.9	2.2

Table 35: Mineralogy of the temperature tests at 140°C and 110°C

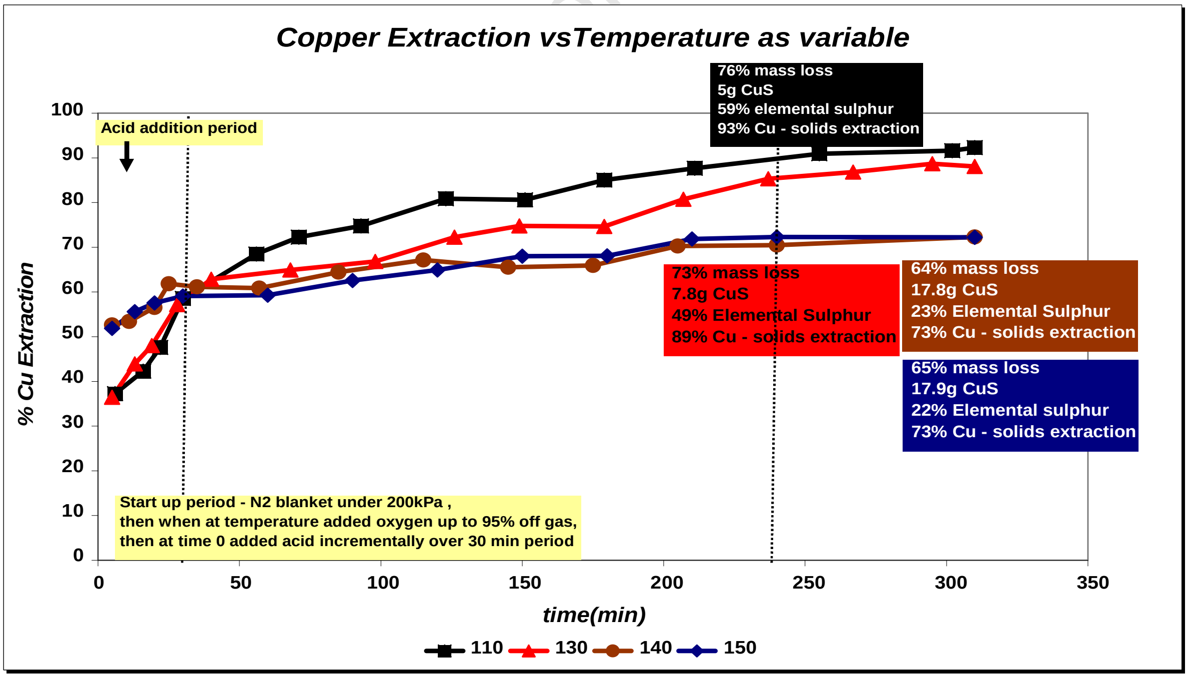
6.5.1 Base metals (Cu, Ni, Fe and S)



Graph 46: Base Metals extraction calculated from solid assays – Varying temperature



Graph 47: Ni extractions calculated from solution assays – varying temperatures



Graph 48: Cu extractions calculated from solution assays – varying temperatures

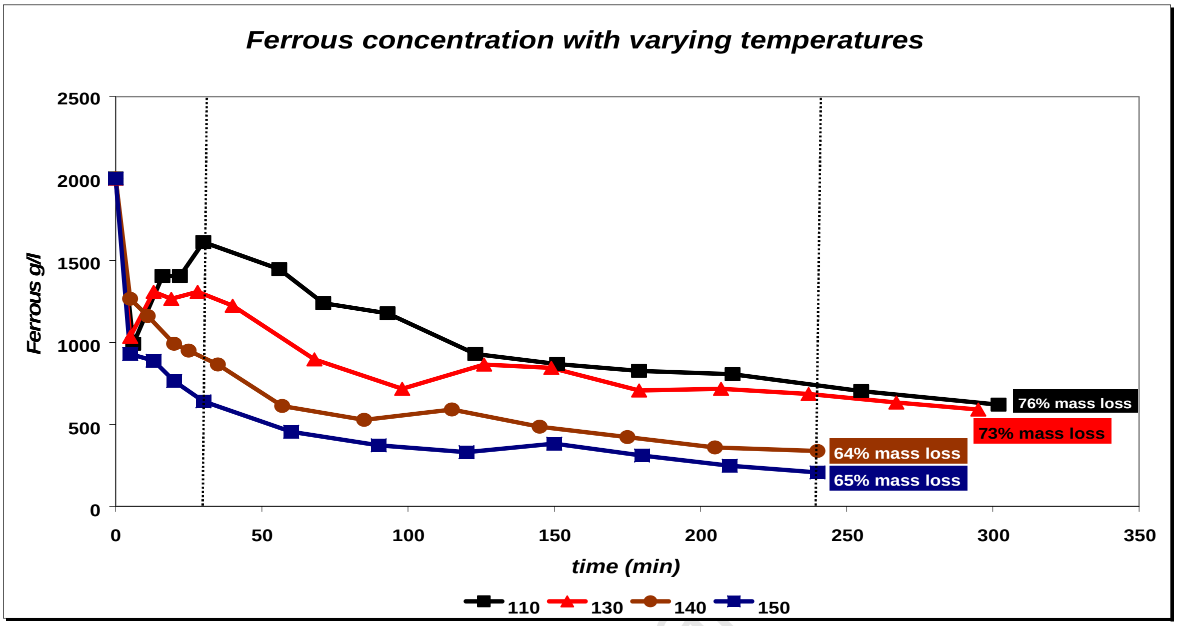
On start up, and as detailed in the experimental procedure, in the absence of acid and oxygen, the ferrous ions in solution will precipitate as a ferrous compound, generating some acid. This acid will immediately be consumed by the hydroxide/ oxide species and partially dissolve. When the reactor is at temperature set point, the oxygen is opened and then acid is added incrementally over a period of 30 minutes.

From the data it appears that at the two higher temperatures, initial dissolution of nickel is approximately 10–20% higher than at the two lower temperature tests **(see Graph 47)**. In all the tests, limited (approximately 7–9%) Ni extraction occurs during the acid addition period (30 minutes). After the acid addition period, further gradual Ni oxidation in the two lower temperature tests is approximately 30–35%, while at the two higher temperature tests it is 10–22%. The initial rate of Ni extraction is much higher at the higher temperatures, but slows down considerably after about 2 hours, while much more gradual Ni extraction occurs in the lower temperature tests, resulting in virtually the same outcome after 4 hours of leaching. Again, at least 60% of Ni leaching occurred within the first 30 minutes.

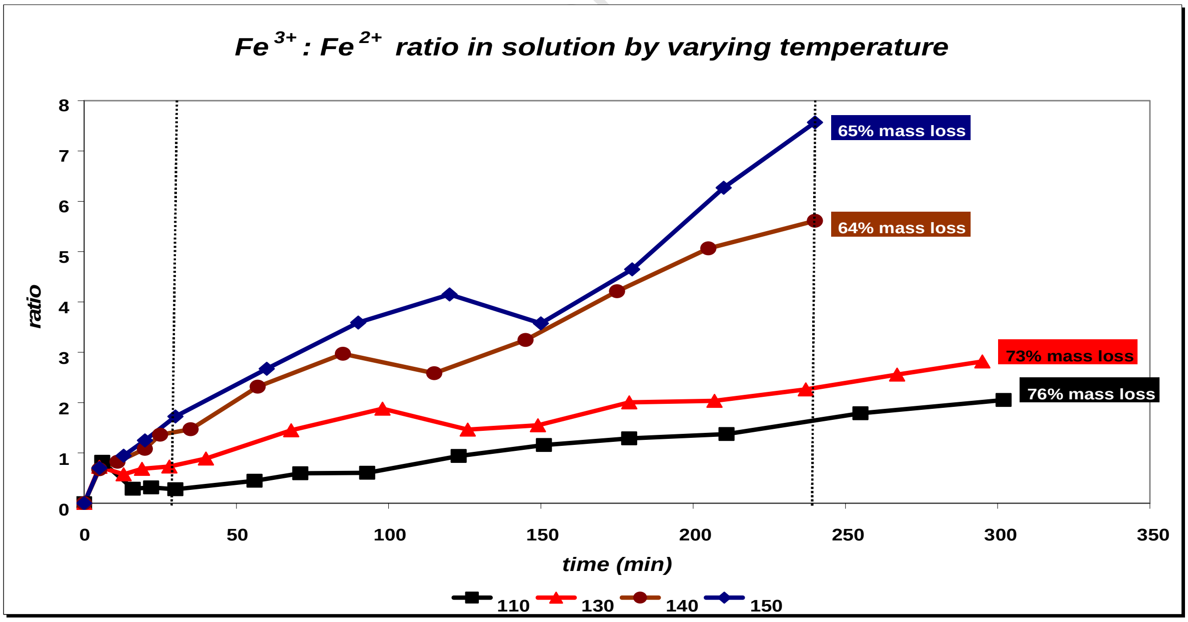
Similarly, for the 110^{o}C and 130^{o}C tests approximately 38% Cu dissolution/extraction has occurred during the heat–up period, another 23% during the acid addition period and approximately 30% further Cu oxidation occurring gradually after this. In the higher temperature tests, 50% dissolution/extraction occurred during the heat up period, only approximately 10% extraction of copper occurs during the acid addition period and a further 10% thereafter. The initial rate of Cu extraction is much higher at the higher temperatures, but slows down considerably, while much more gradual Cu extraction occurs in the lower temperature tests. However, the lower temperature leaches resulted in a much better extraction of copper. Again, in the higher temperature leaches, at least 85% of Cu leaching occurred within the first 30 minutes.

It certainly appears that both the rate and final extent of Ni and Cu extractions are better at 110^{o}C, possibly because elemental sulphur is not in the molten state. According to **Graph 46** during the lower temperature tests the elemental S portion of total S in the final residue is approximately 80–85%, while only about 50% at the higher temperatures. Although the total sulphur extraction is more or less the same, the samples from the lower temperature tests contained much more elemental sulphur.

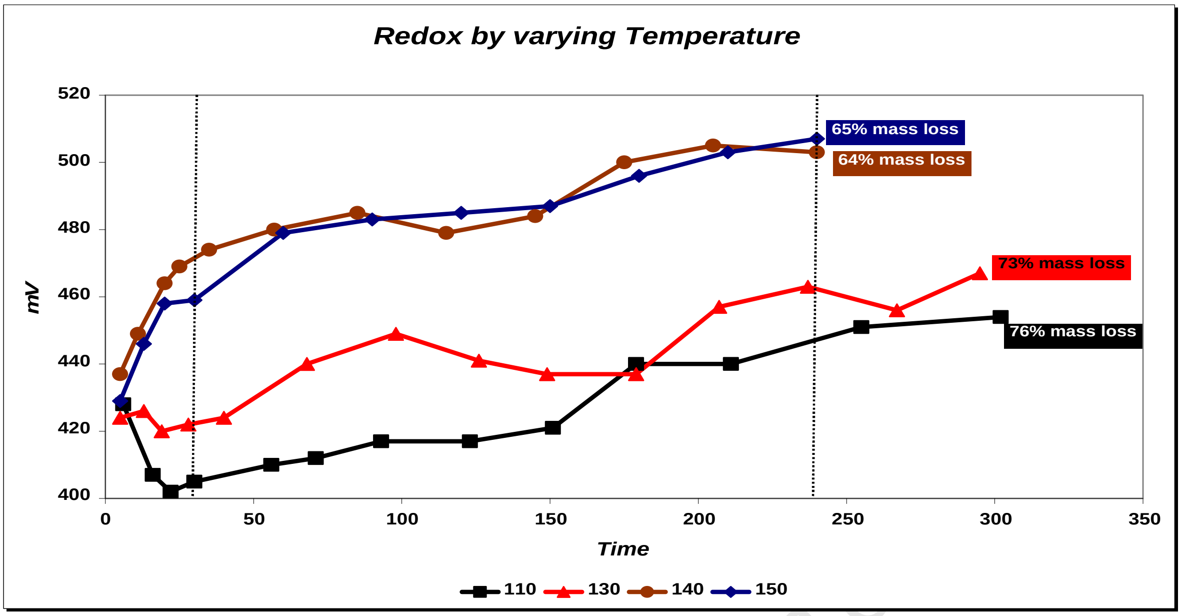
From **Graphs 47 and 48**, Ni and Cu extractions do not appear to be complete after 5 hours of leaching time, and it could potentially improve further if done over a longer period.



Graph 49: Ferrous concentration with varying temperatures

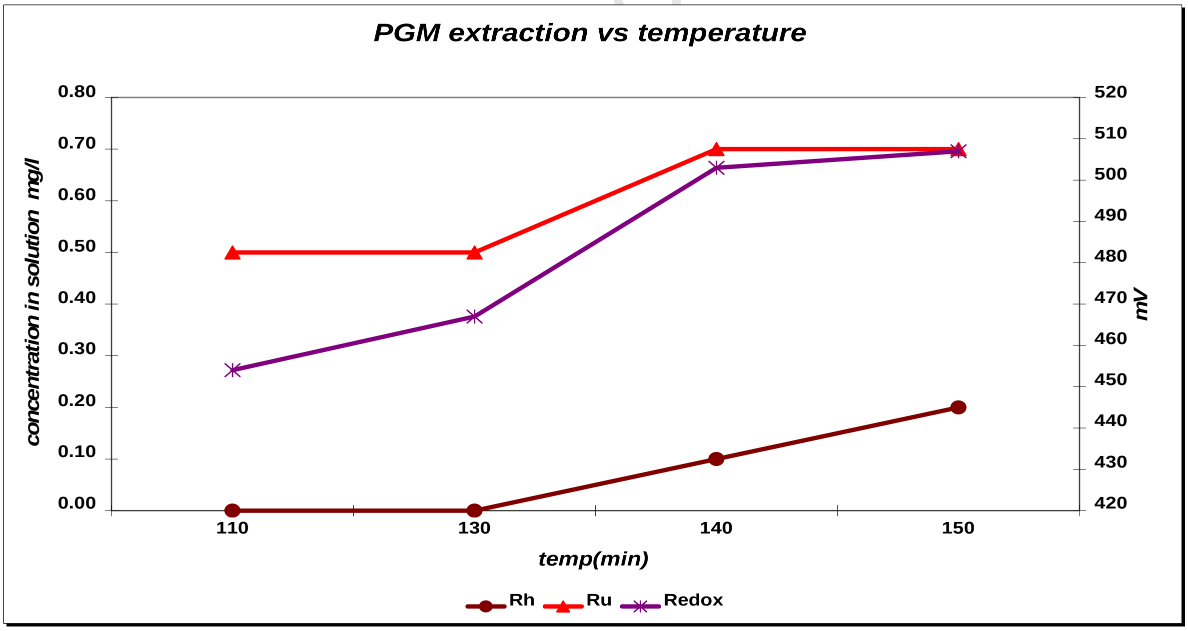


Graph 50: Ferric: Ferrous ratio by varying temperatures



Graph 51: Redox by varying temperatures

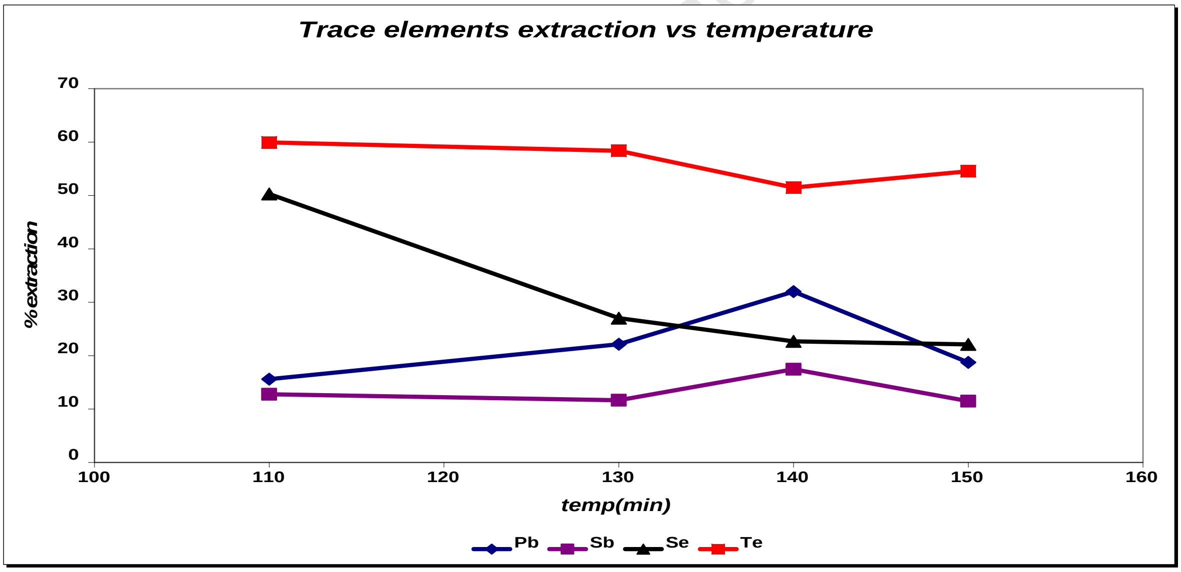
6.5.2 PGMs



Graph 52: PGM concentrations vs. temperature in sulphuric acid leach

When considering the final solution assays on the PGMs, it appears that the higher the temperature, the higher the dissolution of rhodium and ruthenium are. Ruthenium dissolution is in the order of 15% at the lower temperatures, which doubles if the temperature is 140^{o}C and above. Rhodium dissolution also increases substantially with increasing temperatures from around 2% at 110°C to 8% at 150°C. According to literature[28], ruthenium and rhodium dissolution starts occurring around 430mV and Graph 52 shows that the dissolution is definitely related to the redox potential, which in turn is determined by the changing reaction conditions at each temperature, especially the behaviour of Fe. By increasing the temperature, more rhodium, ruthenium and iridium are also dissolved[21] . It also shows that the dissolutions are in the following order, ruthenium > rhodium > iridium. Platinum and palladium dissolution is minimal. These observations are based on solution analysis, and they are extremely low, ie rhodium varies from reported values from the lowest of <0.05mg/l to the highest of 0.2mg/l and for Ru from 0.5 mg/l to 0.7mg/l. However, when calculating this extraction data according to solids assays, there is no PGM extraction.

6.5.3 Trace elements



Graph 53: Trace elements extraction vs. temperature

Selenium extraction is definitely temperature related and the extraction is the highest when the temperature is the lowest . It appears that Se extraction is significantly influenced when elemental S is molten and it seems to exhibit a similar trend as the Cu extractions, ie passivation by molten sulphur appears to play a key role. During the 110°C leach, Se extraction was 50%, while at the other temperatures, when elemental S was in the molten state, Se extractions were only around 22%.

This is contrary to the behaviour experienced by the test work conducted preceding this work[27], where increasing temperature showed increasing selenium concentration. The exact oxidation state of Se was not determined.

Tellurium extraction appears to be between 50–60% and is not really temperature related.

It appears as if there is some Pb and Sb extraction, possibly due to hydroxide species formed during the NaOH leach.

6.6 Mineralogy, General Observations and Results of Oxygen Variation

In order to test the influence of oxygen partial pressure on the NaOH leach residue, three tests were done under the same conditions, but varying oxygen partial pressure:

Temp : 140°C
pO2 : 140, 340 & 540kPa
Agitation rate : 280 rpm
Acid : 30g/l
Fe addition : 2g/l
Leach times : 300 minutes for 140 & 540kPa test
240 minutes for 340kPa test

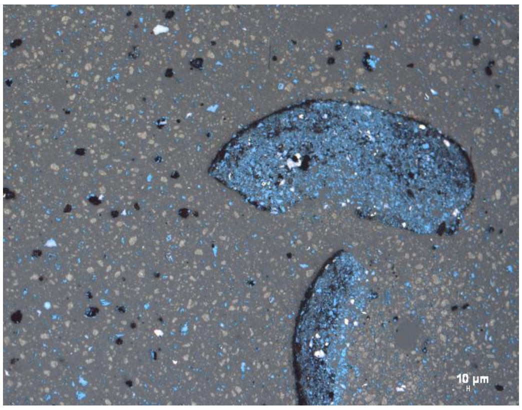
No sulphur balls were observed in the residues during these tests. Unfortunately, during the oxygen variation tests, samples were only taken after the heat up period and only after the oxygen was opened to the vessel in the 540kPa test. However, the start-up regime did not differ much from the previous tests.

The highest mass loss was during the 540kPa oxygen partial pressure test, as shown in Table 38 and **Graph 54**. The 340kPa leach, which was done for 240 instead of 300 minutes, had the highest residual solids mass at the end of the leach, which indicates that extraction is still continuing after 4 hours of leaching. The highest sulphur extraction to sulphate by far was in the 540kPa test. This test also had the lowest proportion of elemental sulphur present in the residue.

The mineralogy on the residues of two of the oxygen partial pressure tests (340kPa and 540kPa) were analysed and the major differences between the residues can be seen in **Table 36**. Although the mass loss difference between the two pressures was 14%, the actual residual covelite concentration at 340kPa and 540kPa was similar. However, the contained sulphur in the two residues differed substantially. The total elemental sulphur in the 340kPa test was 23%, while the test at 540kPa was 13% elemental S, but the 540kPa test was 60 minutes longer. The BM: S ratio for the 340kPa was 0.50, compared to 0.67 at 540kPa, which indicates that more sulphur oxidation took place at 540kPa oxygen partial pressure.

The elemental S contained in the final residue is primarily the orthorhombic type, which is interesting and the amorphous type has not been oxidised at all (although it may have already been oxidised – see explanation in 6.3.1 Mineralogy and General discussion). The starting residue, ie the NaOH residue, had no elemental sulphur present. It is clear from the mineralogy that the higher the oxygen partial pressure, the more sulphur oxidation is taking place. It is also clear from mineralogy that a lot of refractory material appears in the high oxygen partial pressure leach which cannot be explained.

From the MLA maps in Appendix IV, pictures 16 and18, it is apparent that significantly more copper with a much bigger grain size is present in the 340kPa leach. What is interesting though from **Picture 7** is that even in the test where the highest sulphur oxidation occurred, some agglomeration is taking place, although only visible under the instrument. This indicates that when elemental sulphur is molten, sulphur balls begin to form to a certain limited extent.

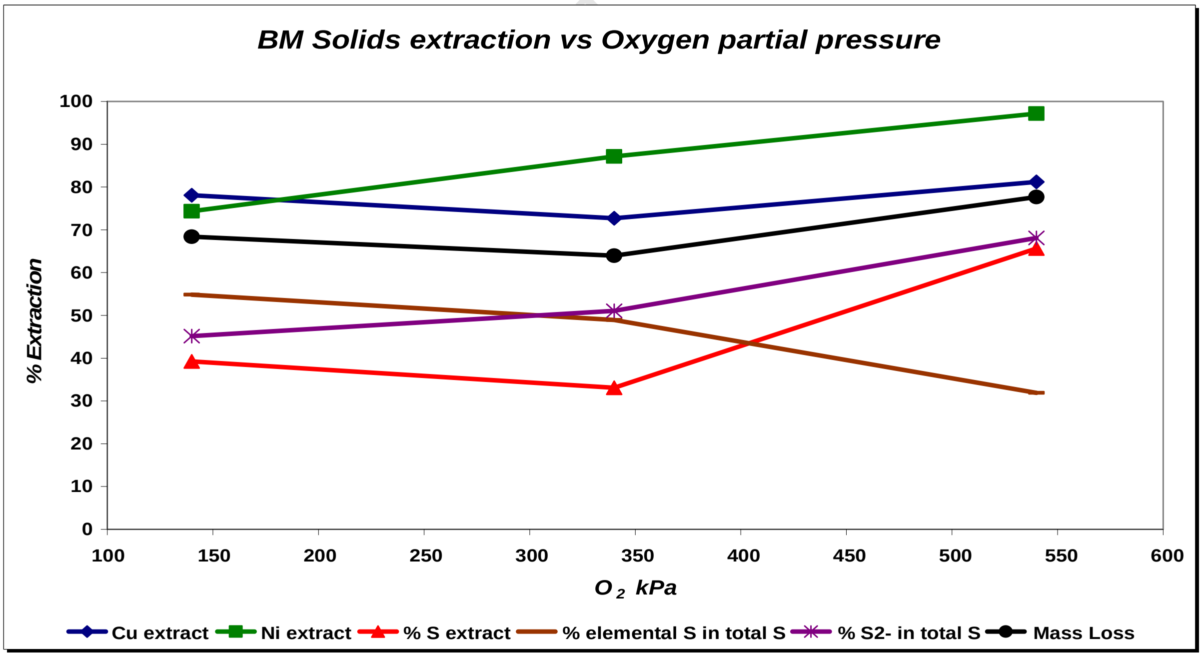


Picture 7: 540kPa test at 140°C with 2g/l initial Fe

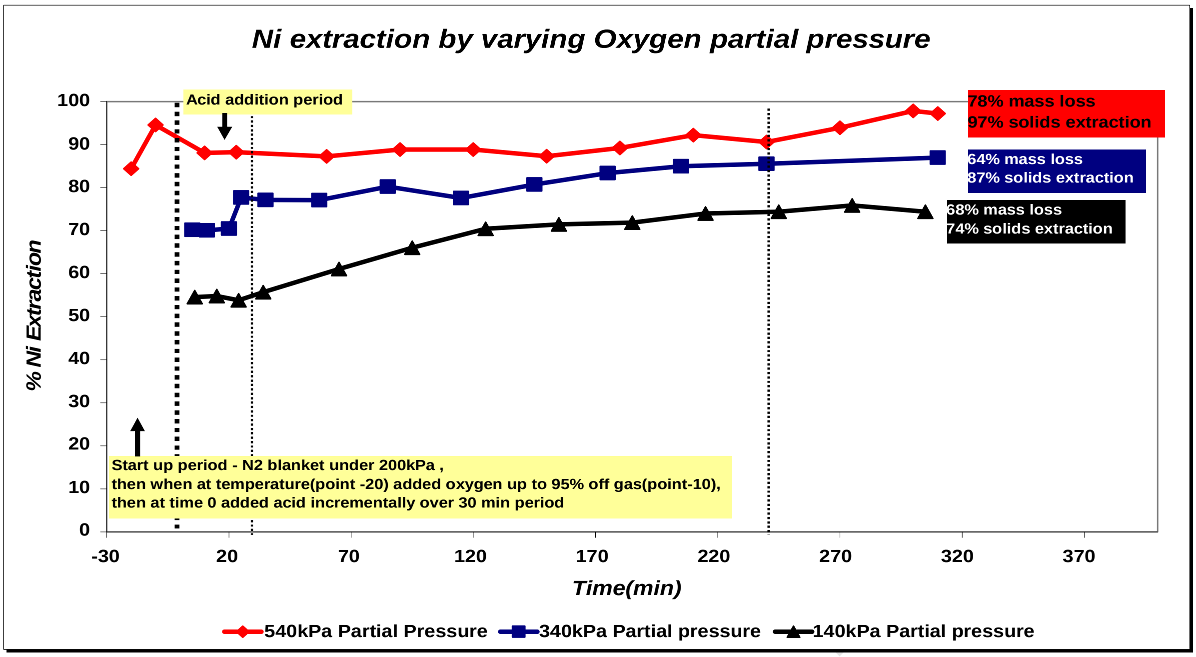
Species	***Residue A after NaOH leach – Initial residue***	***NaOH leach residue after 340kPa pO_2 H_2SO_4 leach***	***NaOH leach residue after 540kPa pO_2 H_2SO_4 leach***
	% Mass		
Covelite (CuS)	74	62	63
Chalcanthite ($CuSO4.5H_2O$)	2.6	0.7	0.2
Tenorite (CuO)	16	0	0
Alt Bornite(close to Cu_3FeS_4)	3.3	3.9	2.1
Fletcherite($CuNi_2S_4$)	3.9	1.6	0.1
Sulphur(S^o) Orthorombic	0	15	5
Sulphur(S^o) Amorphous	0	8	8
Refractory	0.7	0.9	4.5

Table 36: Mineralogy of the 540 kPa pO2 residue vs. initial NaOH residue

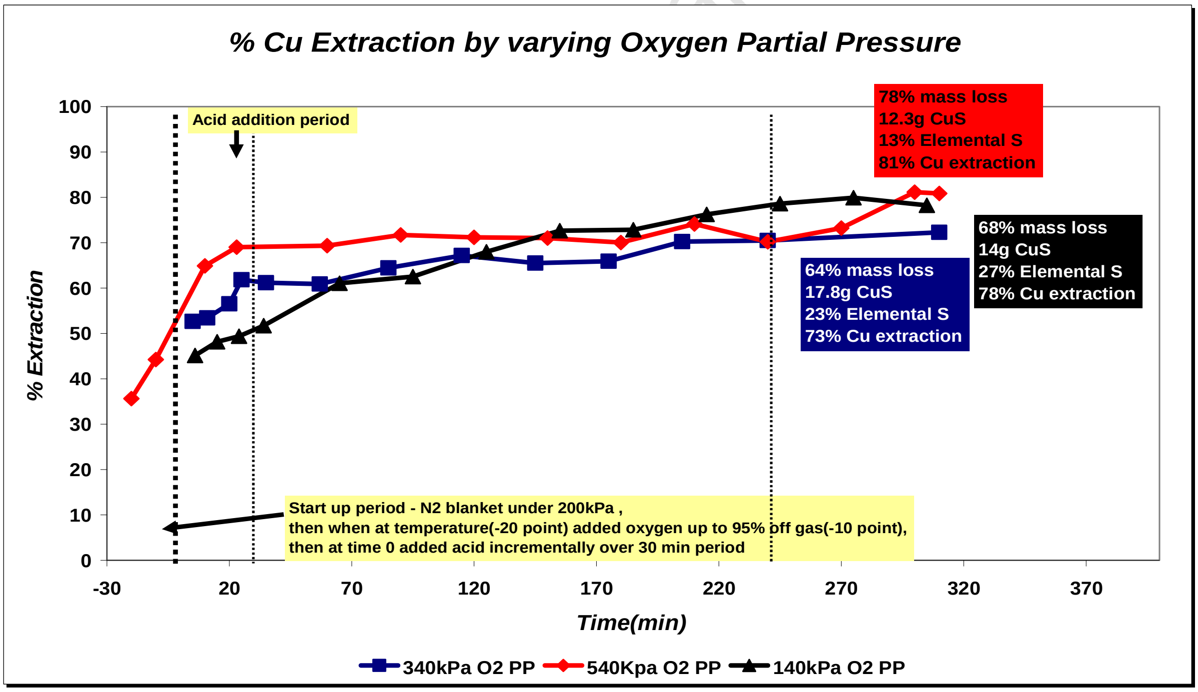
6.6.1 Base metals (Cu, Ni, Fe and S)



Graph 54: Base metal extractions by varying oxygen partial pressures



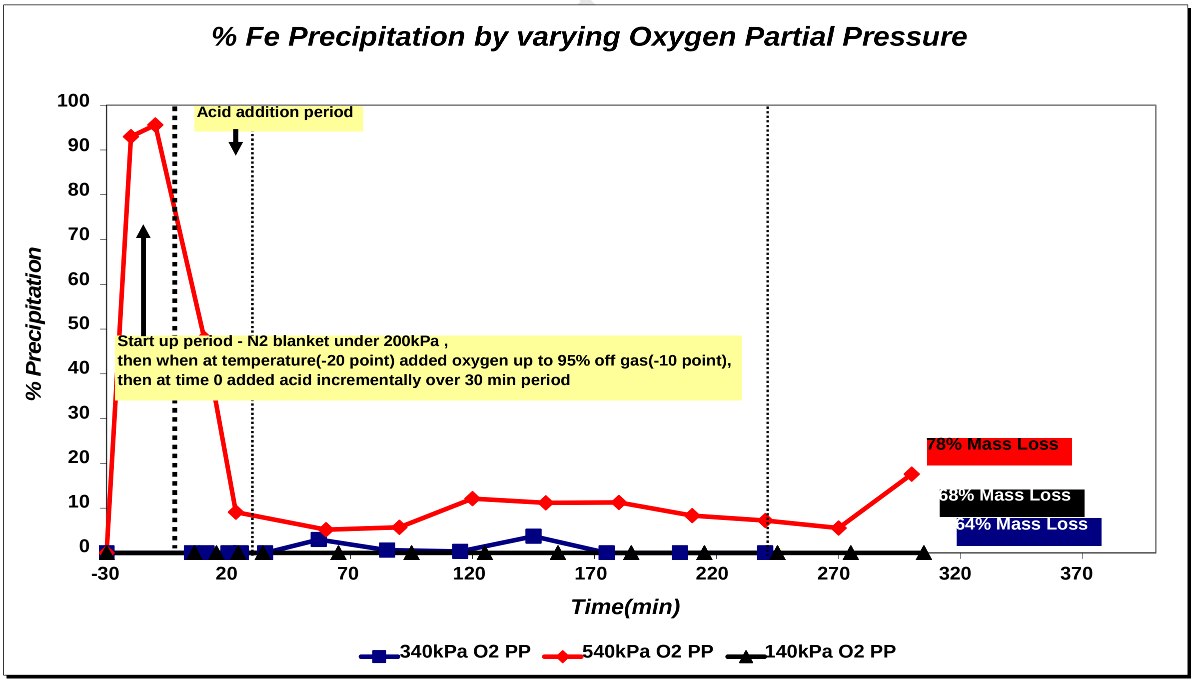
Graph 55: Ni extraction calculated from solution assays by varying pO_2



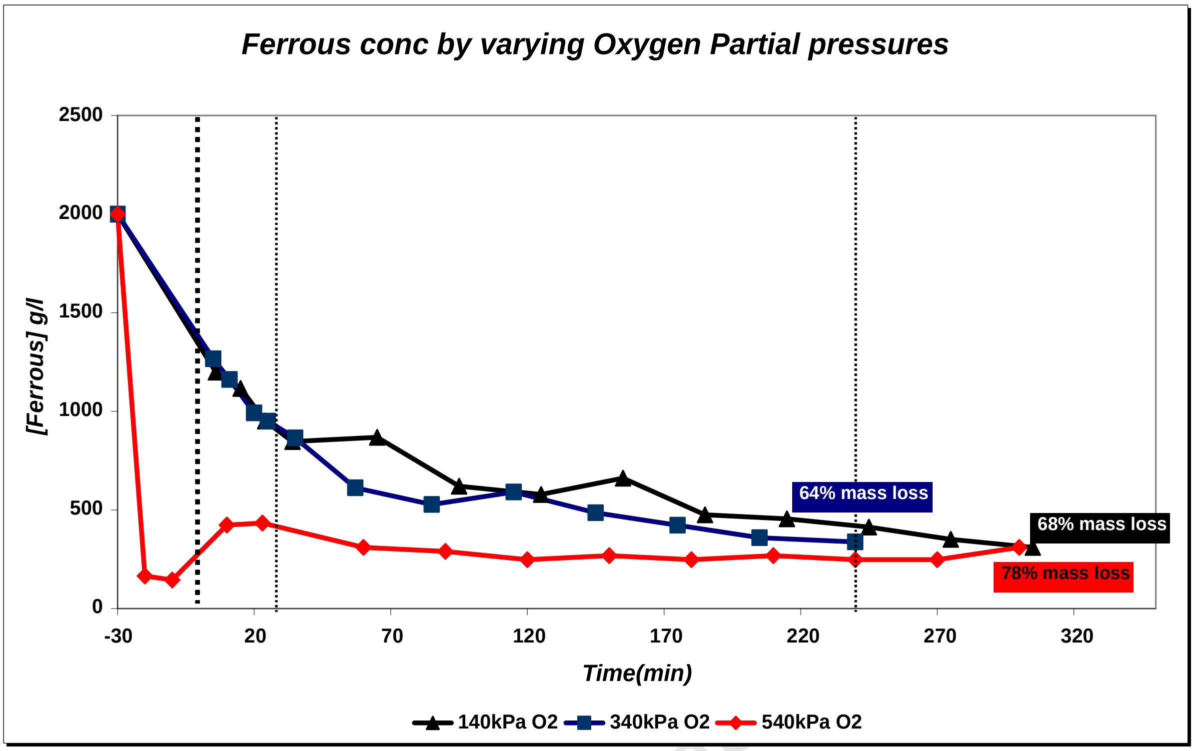
Graph 56: Cu extraction calculated from solution assays by varying pO_2

The test done at 540kPa oxygen was the only test where samples were taken after reaching operating temperature and before any oxygen was added. This indicates that 88% of the nickel dissolves instantly **(Graph 55)**. During the initial stages including the acid addition phase, Ni extraction is better the higher the oxygen partial pressure. It appears from **Graph 55**, that Ni extraction continues in the 140kPa test for approximately 120 minutes but beyond that slows to an extremely slow rate. In the 340 kPa test, there is an approximate 10% increase during the acid addition period, until approximately 30 minutes, and then the same phenomenon happens. In the 540kPa test, there was instant dissolution/ extraction even before any acid or oxygen was added, and it was driven only with temperature during the heat up period. Then, the same phenomenon appears and only after 240 minutes of leaching, does the extraction start increasing again, possibly when most of the elemental sulphur has been oxidised.

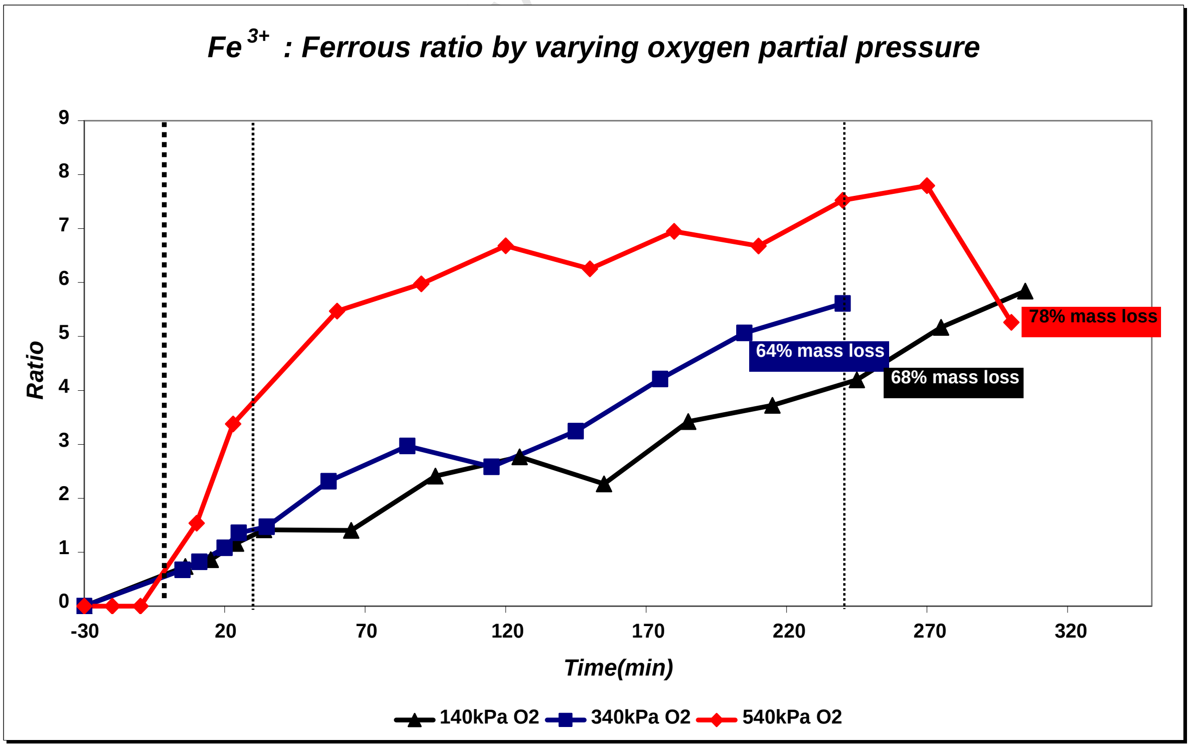
During the heat up period, 35% copper dissolution has occurred, and when the oxygen is opened, the Cu extraction rapidly increases to 45% in the short period it takes for the system to reach steady state gas supply. The acid is then added to the mix, and as explained with Ni extraction above, only after 270 minutes does the Cu extraction start increasing again.



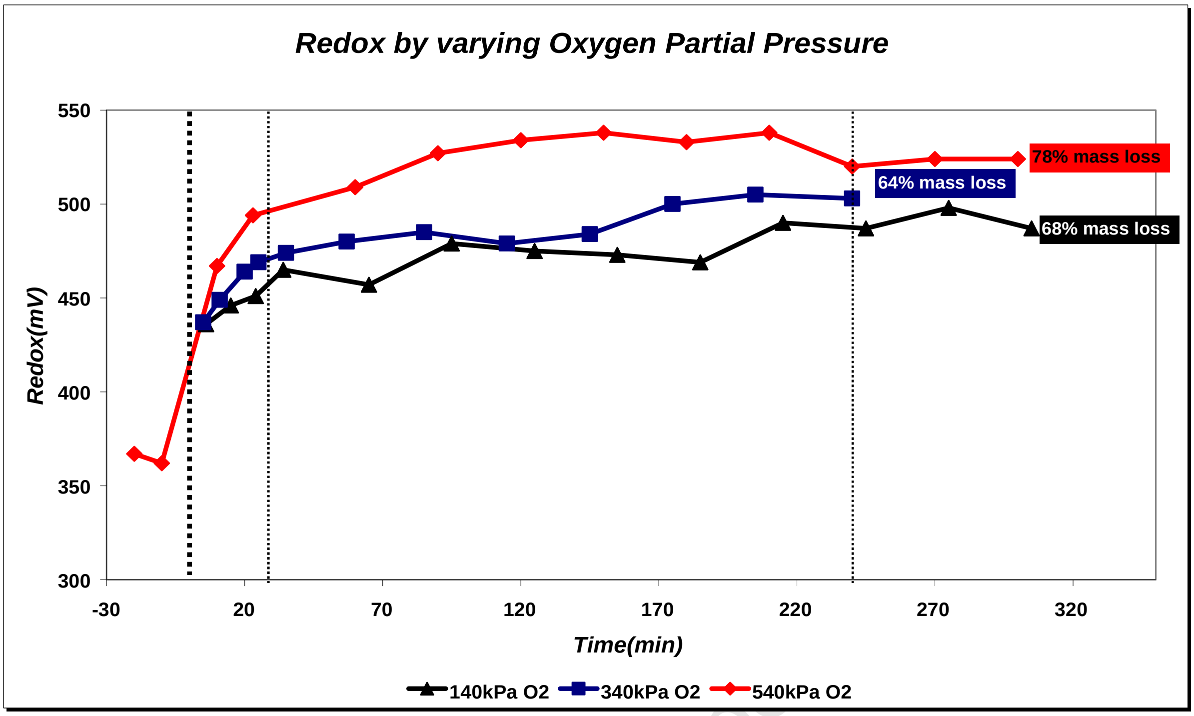
Graph 57: Fe precipitation by varying pO_2



Graph 58: Ferrous concentration by varying pO_2



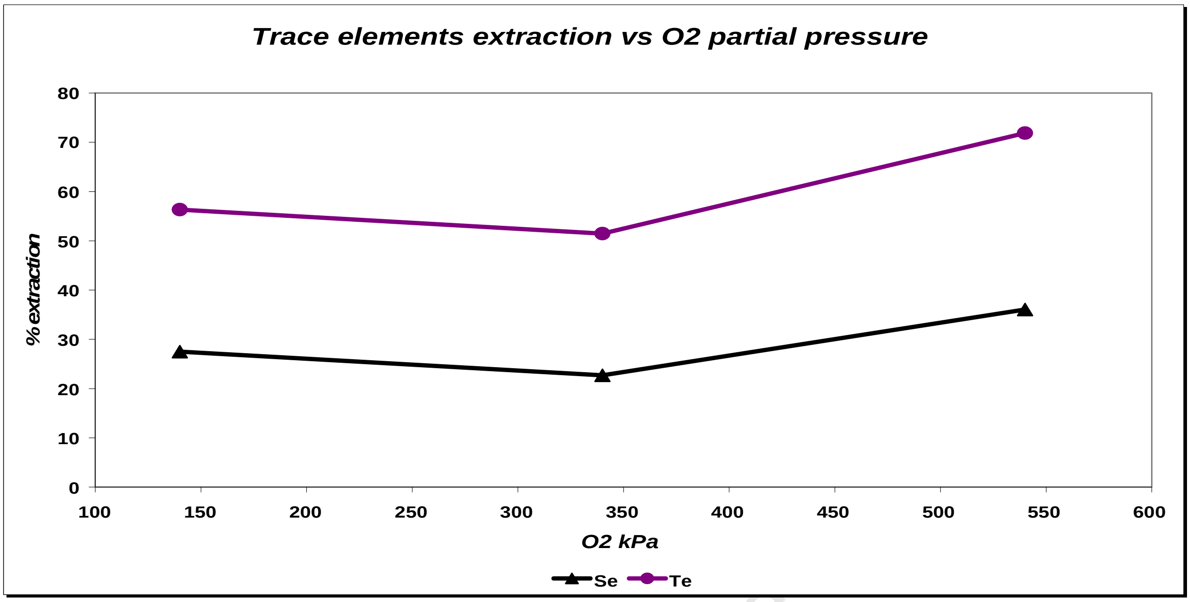
Graph 59: Ferric to ferrous ratio by varying pO_2



Graph 60: Redox change by varying pO_2

Ferrous concentration in solution decreased virtually in the same way during the 140 and 340 kPa oxygen partial pressure tests, but behaved significantly differently with the 540kPa oxygen partial pressure **(Graph 58)**. While getting up to temperature under a nitrogen blanket, the ferrous concentration decreased from 2000mg/l to 150mg/l at 540kPa oxygen. It also decreased for the other two partial pressures, but not as significantly. The ferrous concentration ended at approximately the same value at the end of the leach for all three different partial pressures. The total ferric to ferrous ratio for the three partial pressures also differs significantly during the course of the leach **(Graph 59)** indicating that a lot more ferrous is converted to ferric at the higher oxygen partial pressure. By increasing the oxygen partial pressure, ferrous to ferric conversion is quicker and virtually all Fe precipitates **(Graph 57)** from solution before oxygen and acid are added, and as soon as the acid is added the Fe precipitate re-dissolves fairly quickly. The higher oxygen partial pressure delivered the lower overall residue mass, and therefore the highest overall solids extraction. By increasing the oxygen partial pressures, the redox potential increases more quickly **(Graph 60)**.

6.6.2 Trace elements



Graph 61: Trace element extraction calculated using solids assays by varying the pO_2

The higher the oxygen partial pressure, the more Se and Te dissolves. The test performed at 340kPa was done for a shorter period than the other two tests. Se dissolves between 25–35%, while Te dissolution is higher, between 55–70%.

6.7 Mineralogy, General Observations and Results of Acid Variation

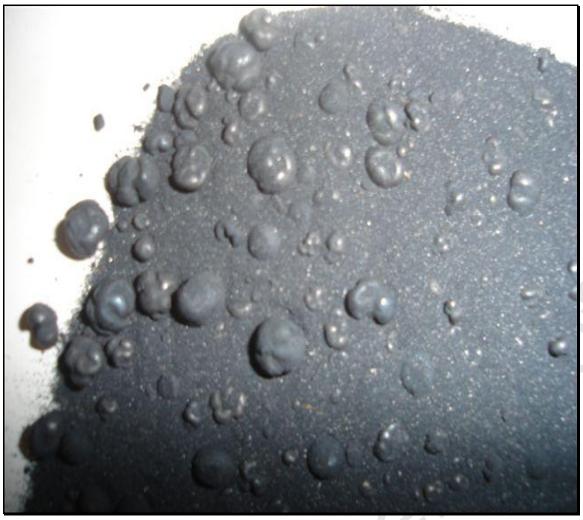
In order to test the influence of acid concentration on the NaOH leach residue, four tests were done under the same conditions, but with varying acid concentrations:

Temp	:	140^{o}C
pO2	:	340kPa
Agitation rate	:	280 rpm
Acid	:	15, 30, 50 & 60g/l
Fe addition	:	2g/l

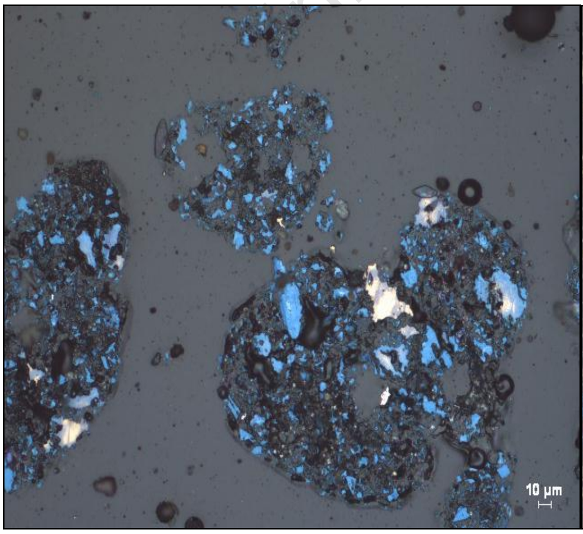
Sulphur balls were noticed in the higher acid leach runs (50 and 60g/l acid) with foaming and slower filtration rates observed. The difference is shown in the leach residues between the

60g/l acid leach **(Picture 8)** and the leach done at 30g/l acid **(Picture 10)**. Unfortunately, during the acid variation tests, no samples were taken immediately after the heat up period, or after the oxygen was opened to the vessel. However, the start up regime did not differ at all from previous tests.

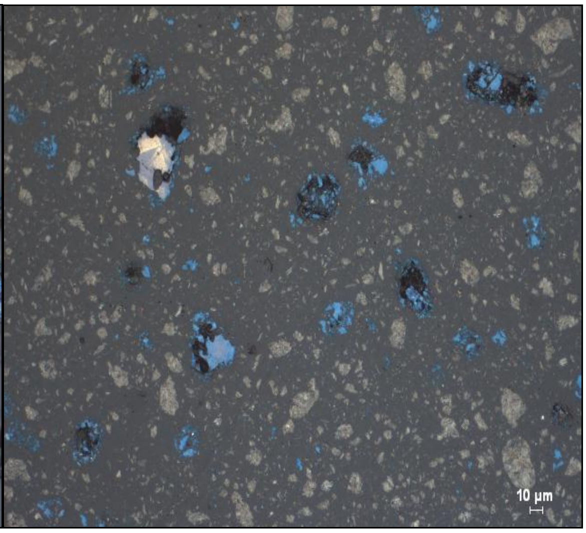
The mass loss between the various acid tests did not vary much as shown in **Table 38** and **Graph 62**. The tests with 15 and 60g/l acid leach conditions extended over 300 minutes, and those with the 30 and 50g/l acid leach conditions for 240 minutes. The highest sulphur extraction to sulphate was in the 15g/l acid test, while the highest elemental S formation was in the higher acid tests.



Picture 8: 60 g/l acid variation



Picture 9: 60 g/l acid test



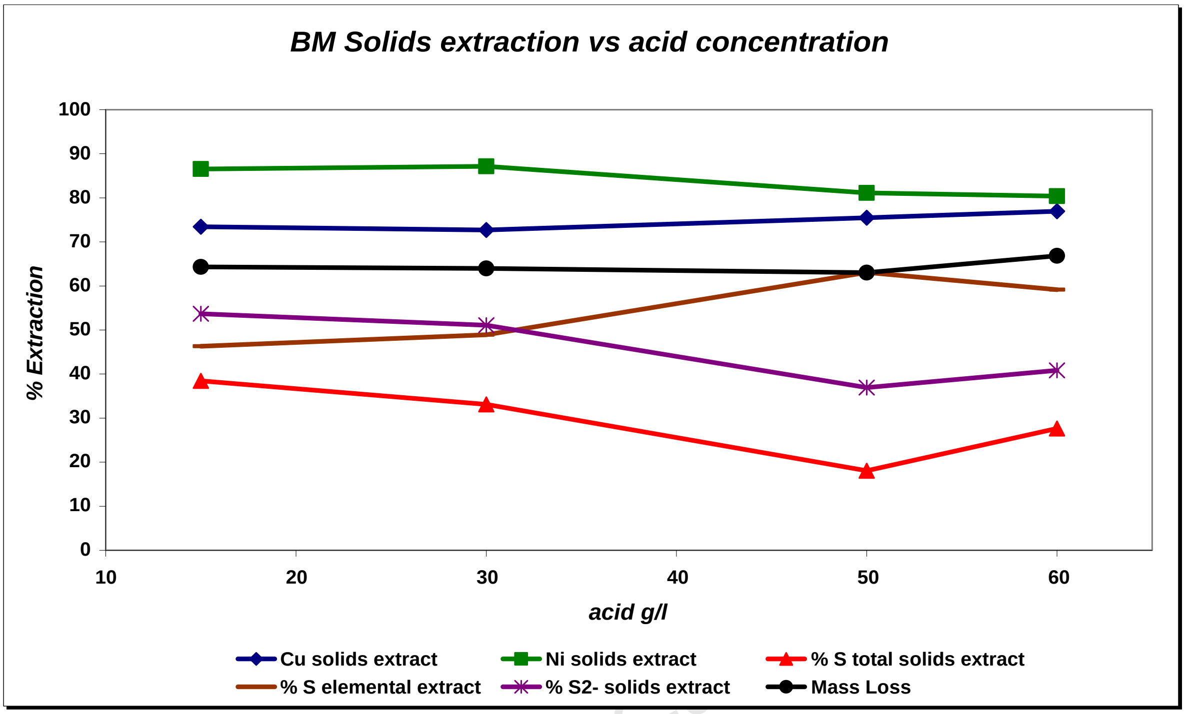
Picture 10: 30 g/l acid test

The mineralogy carried out on the residues of the two acid conditions (30g/l and 60g/l) tested are indicated in **Pictures 9** and **10** and the major differences between the residues can be observed in **Table 37**. Although the mineralogy does not differ significantly when comparing these two acid variations, the sulphur contained in the two residues does differ substantially. The total elemental sulphur in the 30g/l test was 23%, while the test at 60g/l acid was 33% elemental S. The type of elemental S in the high acid test was shown to be all of the orthorhombic type, while the amorphous type was not found (see explanation in 6.3.1 Mineralogy and General discussion). The starting residue, ie the NaOH residue, had no elemental sulphur present. It is clear from the residue mineralogy therefore, that the acid tenor plays a major role in determining the type and quantity of elemental sulphur present in the final residue. From the MLA maps in Appendix IV, comparing Pictures 16 and 19, it is apparent that much bigger grains occurred in the 60g/l leach, with definite sulphur balls forming. This clearly indicates that when elemental sulphur is molten, high acid concentration promotes sulphur ball formation, mainly due to the type of elemental sulphur present, which is the orthorhombic type. Formation of elemental sulphur is a result of the leach conditions in a typical sulphuric acid pressure leach. This is discussed in more detail in section 6.9.

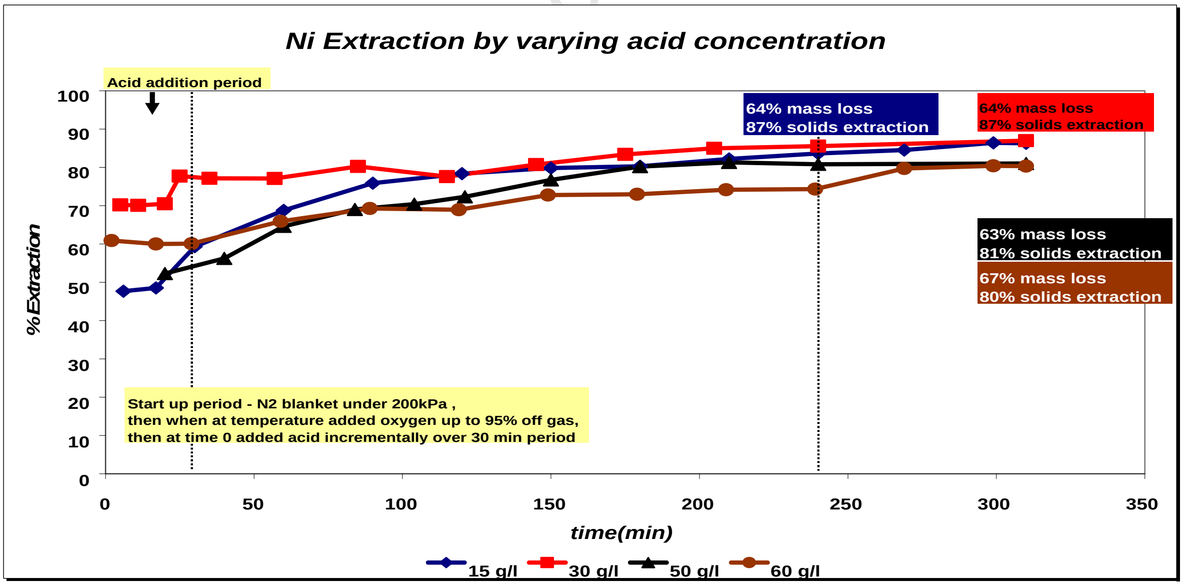
Species	***Residue A after NaOH leach*** ***Initial residue***	***NaOH leach residue after 30g/l H_2SO_4 leach***	***NaOH leach residue after 60g/l H_2SO_4 leach***
	% Mass		
Covelite (CuS)	74	62	58
Chalcanthite ($CuSO4.5H_2O$)	2.6	0.7	1
Tenorite (CuO)	16	0	0
Alt Bornite(close to Cu_3FeS_4)	3.3	3.9	3.9
Fletcherite($CuNi_2S_4$)	3.9	1.6	1.7
Sulphur(S^o) Orthorhombic	0	15	33
Sulphur(S^o) Amorphous	0	8	0
Refractory	0.7	0.9	1.3

Table 37: Mineralogy of the 30 and 60g/l acid and initial NaOH residues

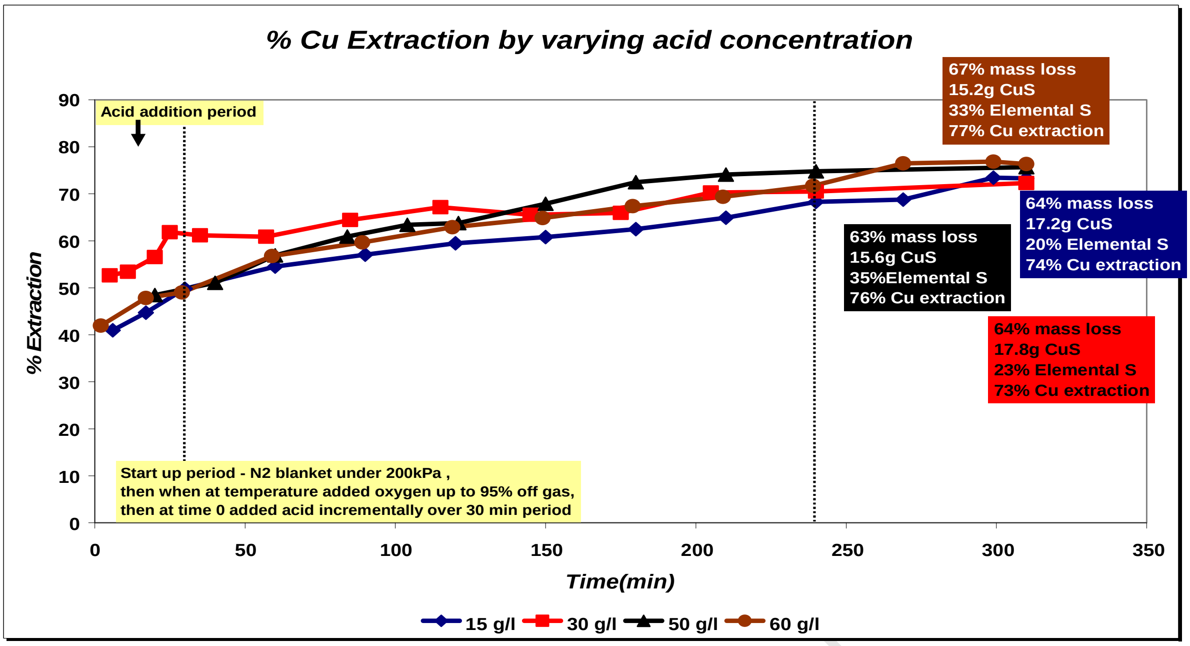
6.7.1 Base metals (Cu, Ni, Fe and S)



Graph 62: Base metals extraction calculated from solids assays by varying acid concentration



Graph 63: Ni extraction calculated from solution assays by varying acid concentration

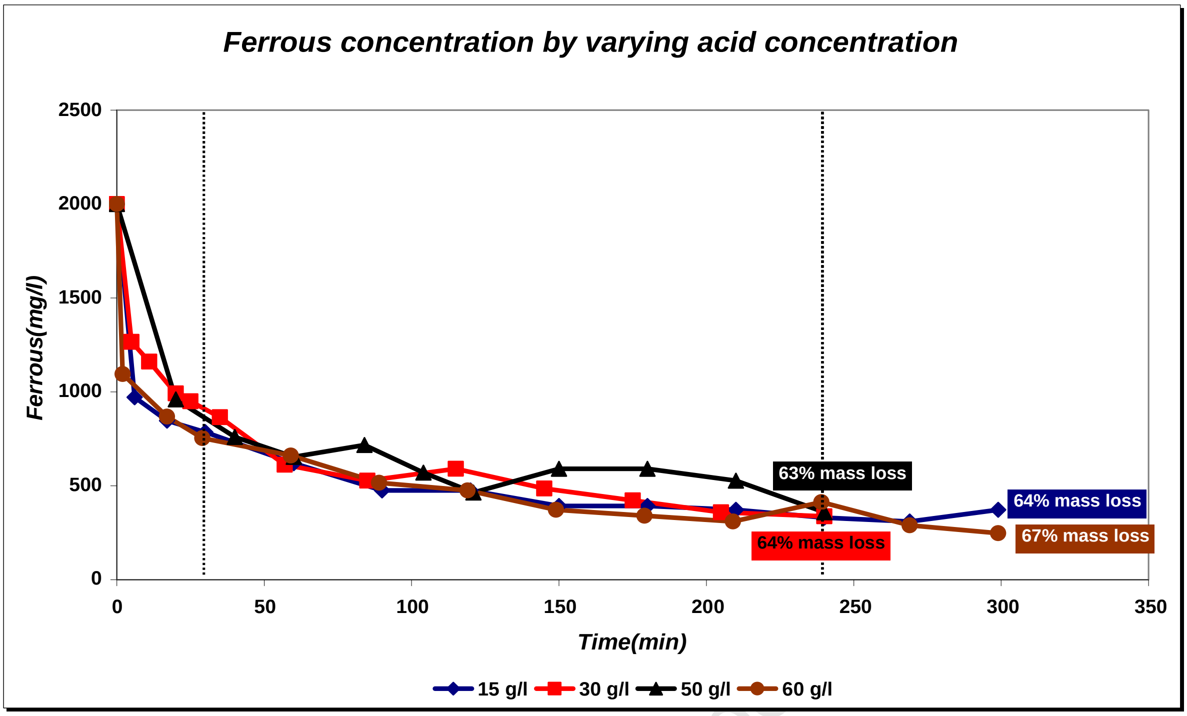


Graph 64: Cu extraction calculated from solution assays by varying acid concentration

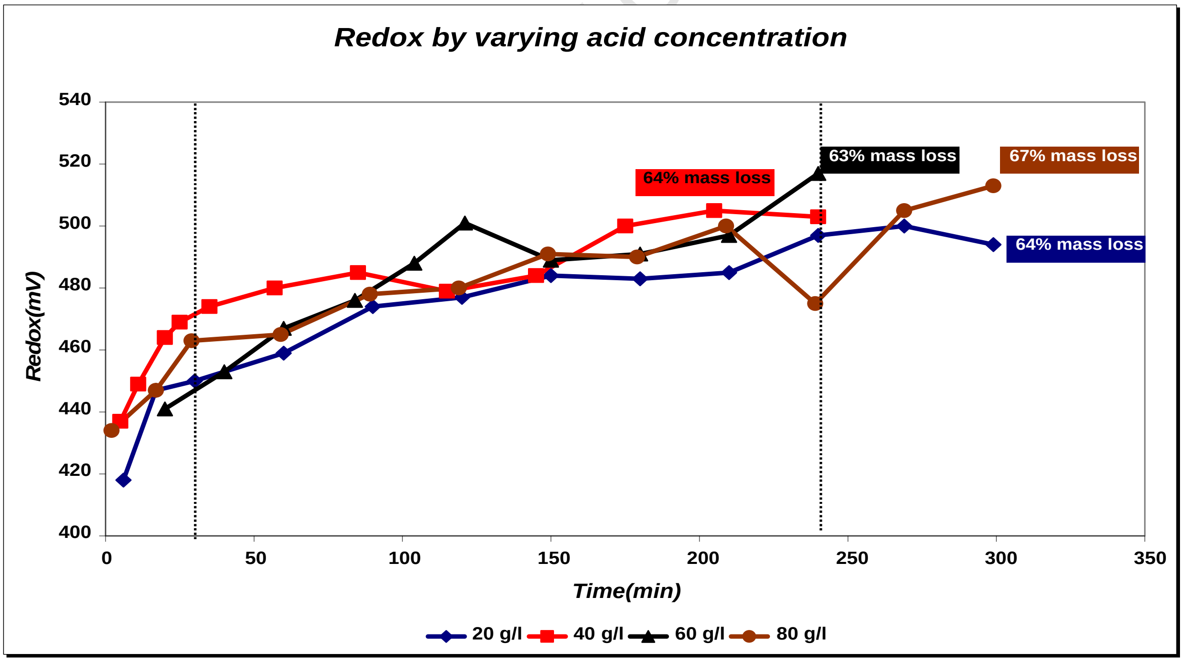
The initial period showed varying degrees of nickel dissolution from 50 to 70%. The final nickel extractions vary between 80–90% and there seems to be only 10 to 20% additional oxidation of nickel after the initial acid dissolution period.

Instant dissolution of copper is between 40–50 % as the acid is added. Another 10–20% extra copper oxidation is achieved after this, going up to a total between 70–80%. There seems to be no significant difference in copper extraction by varying the acid concentration. Increasing the acid promotes the formation of elemental sulphur and inhibits the oxidation of sulphur to sulphate. There appears to be little impact on copper extraction despite the formation of sulphur balls, which is peculiar as it implies higher acid inhibits Ni extraction, yet promotes copper extraction.

Ferrous concentration in solution decreases quite dramatically as soon as acid is added (30–50%) **(see Graph 65)**. After this, it decreases at basically the same rate for all the different acid concentrations, indicating that the ferrous ion is converted to ferric at the same rate, even by varying the acid concentrations. Redox potentials also give no indication that acid concentration has an impact **(see Graph 66)**.

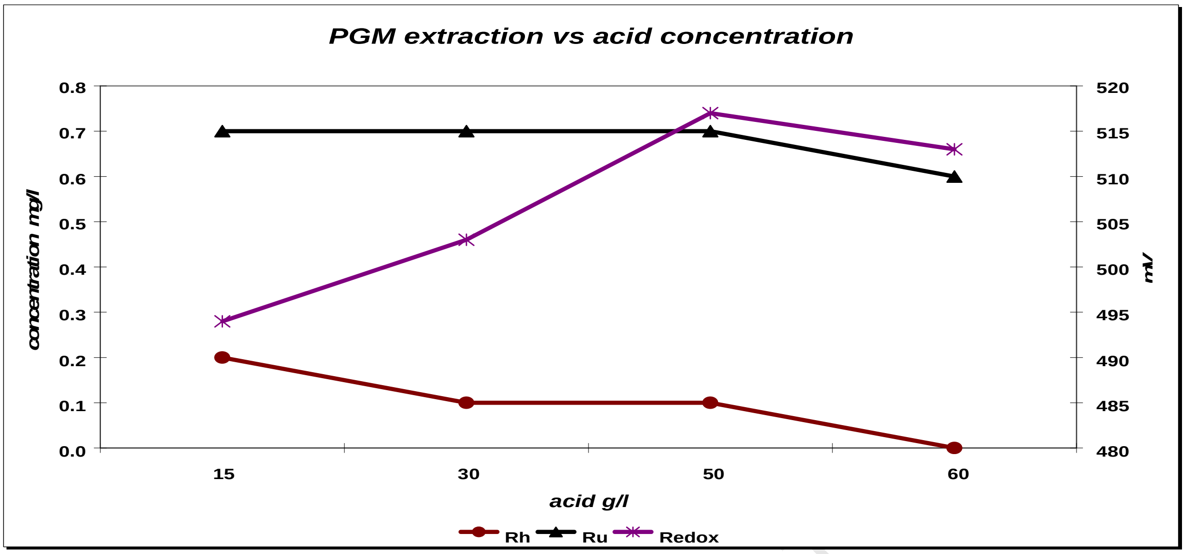


Graph 65: Ferrous concentration by varying acid concentration



Graph 66: Redox by varying acid concentration

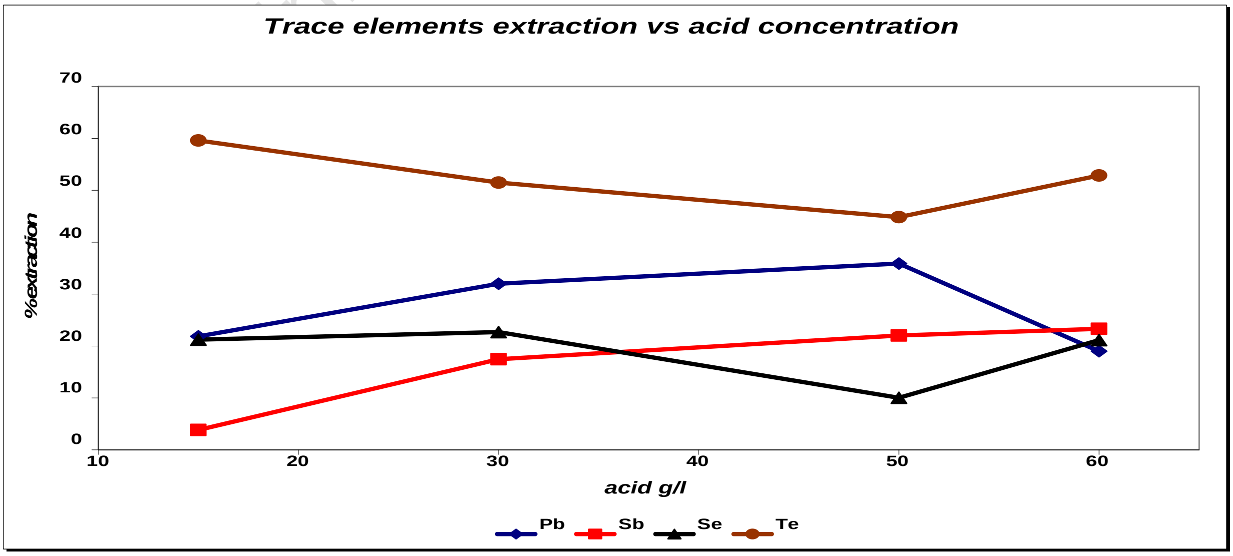
6.7.2 PGMs



Graph 67: PGM concentration vs. acid concentration

The redox increases as the acid concentration increases. The same effect is, however, not seen with Rh and Ru concentrations. It appears as if Rh concentration decreases with increasing acid concentration, but due to the values being so close to the detection limit of laboratory instruments, this observation could be incorrect.

6.7.3 Trace elements



Graph 68: Trace element extraction by varying acid concentration

Lead extractions according to solution assay results are between 20–40%. This is possibly due to the NaOH leach altering the mineralogy of the Pb compound. Selenium extractions are between 10 and 20%, and tellurium extractions between 45 and 60% calculated on solids assays. It does not appear as if increasing acid concentration has any impact on Se and Te extraction.

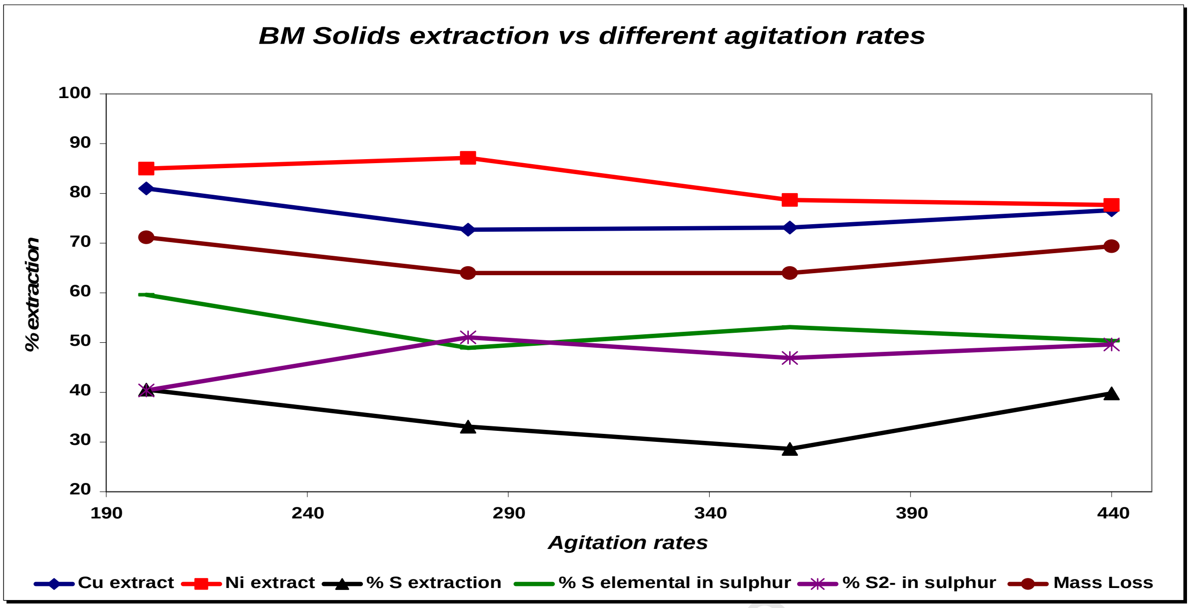
6.8 General Observations and Results from Agitation Rates Variation

In order to test the influence of agitation rates on the NaOH leach residue, four tests were done under the same conditions, but with varying agitation rates:

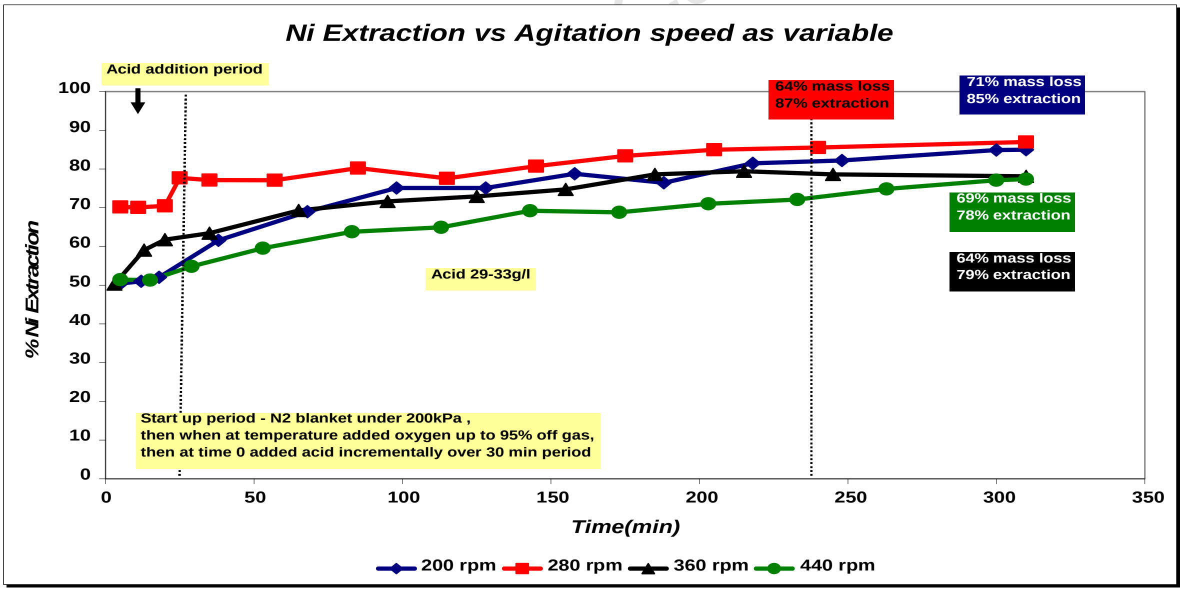
Temp : 140°C
pO2 : 340kPa
Agitation rate : 200, 280, 360 & 440 rpm
Acid : 30g/l
Fe addition : 2g/l
Leach times : 200 & 440 rpm 300 minutes
280 & 360 rpm 240 minutes

As with the temperature variation leaches, the highest mass losses were on the longer leaches, done for 300 rather than 240 minutes. The mass loss difference was in the order of 7% in actual mass. This confirms that there is still some extraction occurring even after 4 hours, possibly copper and oxidation of sulphur to sulphate.

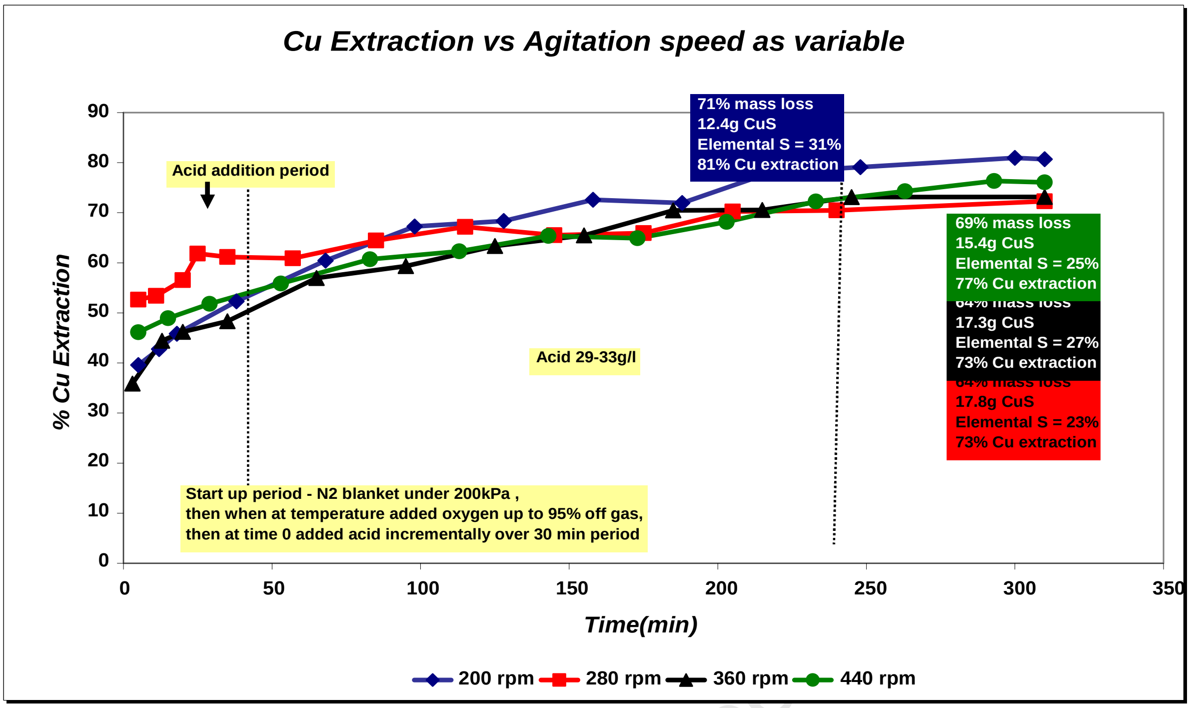
6.8.1 *Base metals (Cu, Ni, Fe and S)*



Graph 69: Base metals calculated from solids assays by varying acid concentration



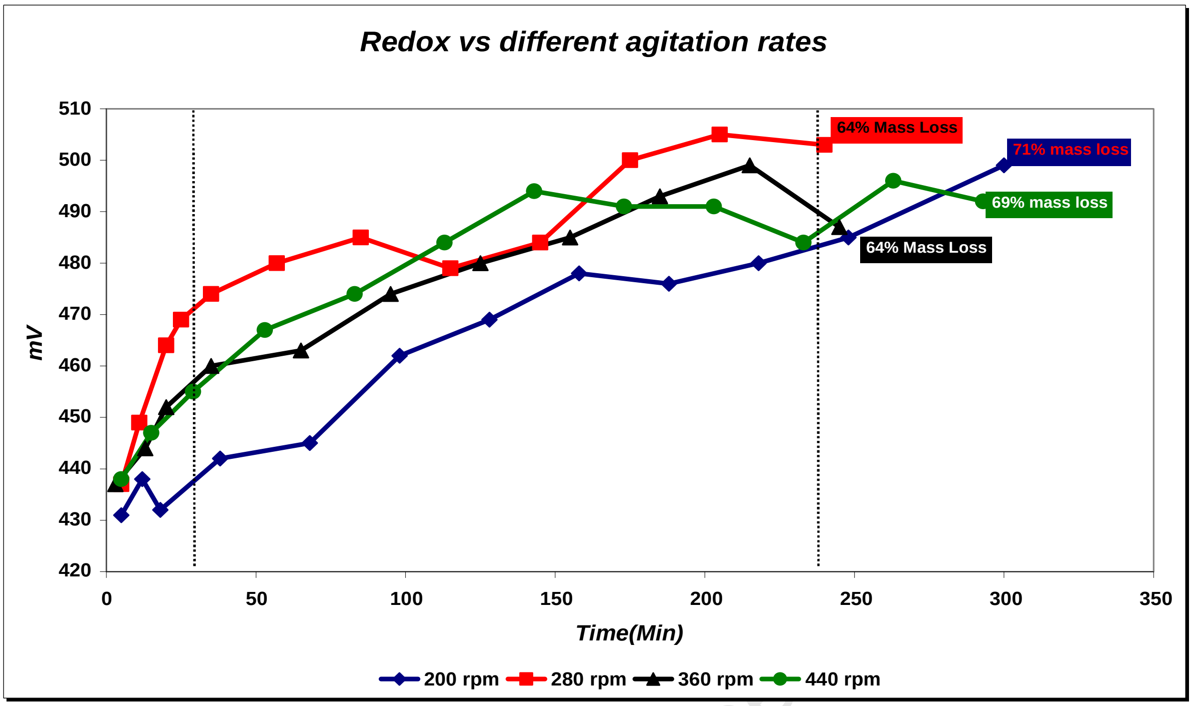
Graph 70: Ni extraction calculated from solution assays by varying agitation speed



Graph 71: Cu extraction calculated from solution assays by varying agitation speed

As with the temperature variation tests, the initial extraction of Ni after acid addition was approximately 50–70%, while copper varied 35–50% **(see Graphs 69–71)**. There does not appear to be any significant difference in extraction if looking at percentage mass loss. The major differences – slightly lower extractions from the tests done at 280 and 360rpm – occur simply because the other two tests were done for 60 minutes longer, but these also indicate that extraction is still continuing after 4 hours. There appears to be no significant difference in Cu and Ni extractions at the different agitation speeds. By running the leach for 60 minutes longer, an extra 4–7% Cu oxidation occurred.

An interesting observation is the fact that there is a slightly better Cu extraction (4%) at the lower agitation rate (comparing the slowest and fastest agitation rates, which were for exactly the same time), although not significantly so. This in itself may not be significant, but this is also coupled with a 10% larger proportion of elemental S in total S in the residue **(see Graph 69)**, and a slightly slower rate of change of the redox potential than during the other tests **(see Graph 72)**.



Graph 72: Redox vs. agitation rates variation

6.9 Discussion of Results

Refer to Tables 38 and 39 and results as presented in the results section from 6.4 to 6.8

6.9.1 General

Nickel extractions varied between 45% and 85% and copper between 6% and 35% during the heat-up phase when the autoclave contents were purged with nitrogen. The ferrous ion hydrolysis generated acid, which could have been partially responsible for this initial Ni and Cu dissolution, but in the test with 0g/l ferrous ions added, there could not have been any acid generated, but Ni hydroxide still dissolved up to 75% and copper up to 6%. It must then be possible that this hydroxide/oxide species, due to the mineralogy changing in the caustic leach, can dissolve in just water. The pH of the initial solution was unfortunately not measured.

However, even if only 6% of the copper dissolved during this heat up phase, due to hydroxides dissolving in acid generated by ferrous precipitation, it would still have been enough to oxidise all the Ni present in the residue because the proportion of Ni in relation to the copper in the residue is small. The mechanism of this reaction would be by metathesis **(refer to Reaction 117)**:

$$\mathbf{6NiS + 9CuSO_4 + 4H_2O \rightarrow Cu_9S_5 + 6NiSO_4 + 4H_2SO_4} \quad \mathbf{(117)}$$

Oxygen addition then commenced without any acid having yet been added, and both Ni (60–95%) and Cu (12–45%) dissolution continued. Further precipitation of Fe occurred (up to 90%) when the oxygen supply was opened to the reactor, driven by the rapid oxidation the Fe^{3+} and subsequent precipitation in the absence of acid.

When acid addition started, all of the Fe which had precipitated started to redissolve. The ferrous concentration decreased continuously during all the leaches, regardless of how much ferrous iron was added initially, and its concentration ended up around 350 mg/l. In the runs where no ferrous was added, the ferrous concentration in solution quickly stabilised around 100 mg/l throughout the leach, which appears to represent an equilibrium in the ferrous to ferric to ferrous conversion cycle. The higher the ferric: ferrous ratio in solution, the higher the redox potentials achieved. The first sample taken during the acid addition period (30minutes), dissolved/oxidised Ni to between 50–70% on average, but during the test at 0 g/l Fe and the high oxygen partial pressure, Ni extractions at this stage were 90%. Cu averages between 40–50% at initial extraction, with the test done at the high Fe concentration extracting 65% Cu. In the last sample, taken during the acid addition period, the Ni extractions varied between 55–75%, while Cu averaged between 50–60%. The abovementioned tests had the best extractions thus far. If the general extraction averages after the acid addition period are compared with the final extractions (**see Tables 38 and 39**), it is very evident at this stage that after the acid addition period, between 70–75% of the total extractions achieved on both these elements has occurred already.

From the results described, it is apparent that the presence of elemental sulphur has a major impact on the extraction of most of the elements described. The melting point of elemental sulphur varies and the type of elemental sulphur will determine its melting point. Nontheless, it can be accepted that, as stated by Dreisinger [23] due to the slow increase in temperature during the heat-up period, the melting point of elemental sulphur would be approximately 119°C. During the temperature variation tests, tests were done both below and above this melting point. Below the sulphur melting point, elemental sulphur cannot influence the sulphide leaching in a negative manner, because it would not coat particles and thereby restrict oxidant migration to the particle surface. It certainly appears that both the rate and final extent of Ni and Cu extraction are better at 110°C, possibly when elemental sulphur is not in the molten state.

There are two oxidants at work during this test work, ie oxygen and Fe. To explain the influence of temperature on the oxidation of sulphur and sulphides, it is necessary to highlight some important literature findings

Oxidation of sulphides with oxygen

Molten elemental sulphur is oxidised to sulphate ions with time, temperature and oxygen partial pressure, as is explained by the theory and test work done by Habashi & Bauer[23], who studied the oxidation of elemental sulphur in the temperature range 60–170°C,

$$S + 3/2\ O_2 + H_2O \rightarrow H_2SO_4 \qquad (118)$$

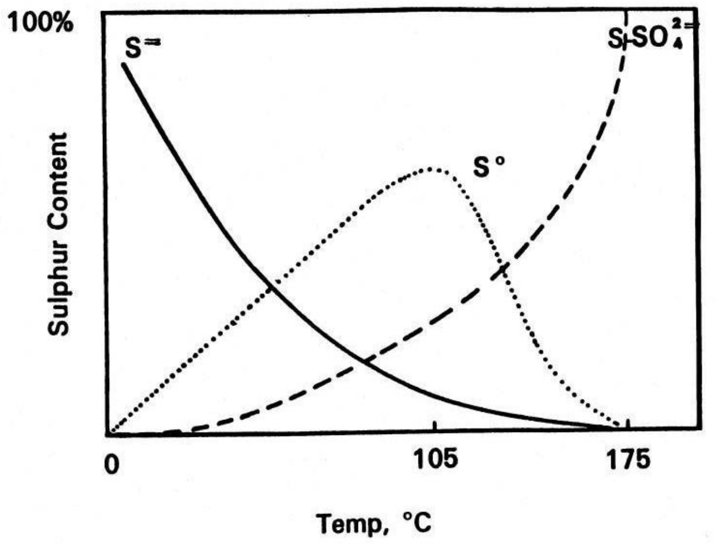
Reaction 118 depends largely on temperature and oxygen pressure. The rates were only appreciable above the sulphur melting point (119°C), and then increased with increasing temperature. Therefore, the following three reactions can be dominant depending on the temperature and oxygen partial pressure,

$$S^{2-} + 2O_2 \rightarrow SO_4^{2-} \qquad (119)$$

$$S^{2-} + O_2 + 4H^+ \rightarrow 2S^0 + 2H_2O \qquad (120)$$

$$S^0 + O_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ \qquad (121)$$

From **Figure 7**, it is apparent that temperature does play a major role in sulphur oxidation to sulphate, and the lower the temperature, the less the sulphur oxidation to sulphate takes place.



Oxydation of sulphides at pH≤3
(From Metallurgical Reviews 1966 vol. II, p. 143)

Figure 7: Oxidation of sulphides below pH 3

Oxidation of sulphides with ferric

Dobrokotov[28] in the study of the pressure oxidation of base metal monosulphides in the presence of Fe suggested the following mechanism.

$$4Fe^{2+} + 4H^{+} + O_2 \rightarrow 4Fe^{3+} + 2H_2O \qquad (122)$$

$$2Fe^{3+} + S^{2-} \rightarrow S^{0} + 2Fe^{2+} \qquad (123)$$

$$6Fe^{3+} + S^{0} + 4H_2O \rightarrow 6Fe^{2+} + 8H^{+} + SO_4^{2-} \qquad (124)$$

$$8Fe^{3+} + S^{2-} + 4H_2O \rightarrow 8Fe^{2+} + 8H^{+} + SO_4^{2-} \qquad (125)$$

Reaction (122) needs to take place before any ferric ions can play a role in the oxidation process. Thermodynamic analysis of above reactions shows that high acidity, low temperature and low oxygen partial pressure will favour reaction (123), whereas decreasing acidity and increasing temperature and oxygen partial pressure will shift the reaction mechanism in favour of the direct oxidation of sulphide ion to sulphate ion (125). At temperatures ≤ 130°C, reaction (125) does not take place below a redox of 500mV.

6.9.2 *Discussion on ferrous variations*

All the ferrous concentration variation tests were done at a temperature of 140°C, which is well above the sulphur melting point, and it is expected that the mechanism should swing in favour of **reaction 119** and **125**.

During the start up period, ie putting the autoclave under nitrogen pressure and heating to the required temperature, a time of about 25 minutes, the ferrous ion concentration in the solution drops by approximately 40% due to precipitation as hydroxides. The acid which forms as one of the products during this precipitation dissolves some of the hydroxides/oxides of copper and nickel which are present in the mineralogy of the NaOH residue. The action of copper on nickel by the metathesis reaction is clearly illustrated in **Reaction 126** below,

$$6NiS + 9CuSO_4 + 4H_2O \rightarrow Cu_9S_5 + 6NiSO_4 + 4H_2SO_4 \qquad (126)$$

in which the stochiometric amount of copper dissolved was enough to oxidise all of the nickel present in the residue. Yet only 45% of the nickel was dissolved.

In the one test where no ferrous ions were added to the mix, no acid could have been generated from the precipitation of Fe and none of the hydroxide components should have dissolved. However, 380 mg/l of Cu, ie 6.3% Cu did dissolve, but the mechanism by which it happened is not clear. As stated earlier, even this would have been enough to oxidise all of the Ni present in the residue, and it actually dissolved 75%. The metathesis mechanism generates 4 moles acid for every 6 moles Ni extracted, which would likely have an effect due to its high concentration in the vicinity of the Ni particles. This, in the presence of Fe, would promote the formation of elemental S, which would coat the Ni particle surface. This effect is most probably already taking place in the early stages of the leach, as can be seen in the large difference of Ni extractions when ferrous is added and when not. It must be kept in mind that oxygen is not supplied to the reactor at this stage and that the autoclave remains under a nitrogen blanket.

When oxygen supply is started, the Fe precipitates even further to approximately 80%, partially ferrous already precipitated, and partially ferric formed after oxygen addition. This generates enough acid to oxidise almost 80% of the ferrous to ferric ions and dissolve base metals in hydroxide/oxide form. In the presence of oxygen, the oxidative power of the solution was enough to dissolve 35% of the copper in the 3 g/l ferrous addition test. By comparison the 0 g/l test could only have generated a very small amount of acid, therefore taking the ferric ions as oxidant largely out of play **(Reaction 123 and 125)**. Still some 13% Cu was extracted, and this could purely have been due to **Reaction 119 and 120**. The reason why oxygen is a slower oxidant in these tests is because oxygen dissolves into the solution only to a few mg/l, while there is such a vast amount of ferric ions available as oxidant in the 3g/l test. The benefit is that when no Fe is present at this stage, the formation of elemental S is largely eliminated.

When the acid addition phase starts, acid is added to the leach in increments over the next 30 minutes. At 0g/l ferrous ion addition, the predominant reaction is **Reaction 119**. This is indicated by the molar BM: S ratio in the residual solids of 0.78, which means that most of the sulphur had been extracted into solution as sulphate ions and the total S extraction into solution is by far the highest of all of the tests done (**see graph 37** and **Table 38**). The little bit of S left in the solids is mainly present as sulphides with only 23 % of the S present as elemental sulphur, ie 8% elemental S in total solids. This is significant, because it shows that in the absence of Fe as another possible oxidant S extraction into solution is more complete, and the formation of elemental S is limited.

This then raises the question of why the addition of Fe promotes the formation of elemental S (**Reaction 123**). A possible explanation is that all the reactions of ferric where the S^{2-} or S^{o} is oxidised to sulphate will generate acid and result in a high acid concentration surrounding or in close proximity of the particles being oxidised. It is a well-known phenomenon that high acid[27 & 28] concentration promotes the formation of elemental S. On the other hand, all the reactions in which sulphides are oxidised to elemental sulphur consume acid, and this same effect will not be appearing.

In the case where elemental S formation is limited (0g/l Fe test), the assumption can be made that an elemental S surface layer around the particles would be virtually non-existent or only very thin. Diffusion of oxygen as the only oxidant to the particle surface would be a lot quicker and better reaction rates can be achieved. The oxidant is therefore not consumed in the reaction to oxidise elemental S to sulphate sulphur in the surface layer because the surface layer contains very little elemental sulphur, and less oxidant overall is required to achieve the same outcome. This is the reason why extraction results were better in the 0g/l Fe test. The highest Cu extraction resulted and also the highest mass loss for all of the tests done at 140°C in the 0g/l Fe test.

When Fe is added to the mix at 1 g/l, sulphur extraction to sulphate immediately drops from 75% to 43% and the elemental S portion of the total remaining S has increased to 33% **(See Table 38)**. Increasing Fe to 2 g/l, sulphur extraction to sulphate drops even further to 33% and the elemental S portion of the total remaining S has now increased to 49%. This shows that although **Reaction 119, 122 and 125** is still happening, **reactions 120 and 123** are becoming much more prevalent. Because of this, the elemental S layer around the particles increases in thickness and the subsequent diffusion rate of oxygen and Fe acting as electron carriers will slow down through this layer. Also **reactions 121 and 124** in and around the surface layer will diminish the extra oxidation power which should have been delivered by the addition of ferrous ions, thereby diminishing the extraction of Cu. This is the case, because Cu extraction has now decreased from 83 % (0g/l Fe) to 69% (1g/l Fe), and the mass loss has decreased from 82% to 70%.

By increasing the Fe to 2 g/l, this elemental S surface layer around the particles increases and diffusion will slow further. The molten elemental S in the mix is greater and will deplete the extra oxidant which should have been delivered by the addition of ferrous ions, thereby diminishing the extraction of Cu. This, however, reaches a turning point at 2 g/l Fe addition, and because of the extra ferric ions now available, more ferric ions will progress through the surface layer because of the concentration effect, and more Cu would be extracted, which is indeed the case as Cu extraction has now increased from 69% to 73%. The rate of elemental S generation, the rate of Cu extraction and the rate of elemental S oxidation to sulphate reaches a point between 1 and 2 g/l Fe addition, where it is in balance and this is the reason why Cu extractions started to increase.

Now, by increasing Fe even further to 3 g/l Fe, the sulphur extraction suddenly starts to increase again and the elemental S portion of total S starts decreasing. This is not an indication that **Reactions 120 and 123** are no longer the more prevalent reactions, but rather an indication that the combined oxidation power of oxygen and ferric ions acting as electron carriers is now a lot more and that the rate at which elemental sulphur generated around the particles is oxidised to sulphate ions has exceeded the rate at which elemental sulphur is generated from **reactions 120 and 123**. This does not mean that suddenly a better Cu extraction will result, although eventually with time it should, rather it means that S extraction into solution will be better and less elemental S will be in the residue. This indeed is the case, because elemental S in the total S portion of the residue has now decreased to 33%.

With the above in mind, it can be said that better total Cu extractions will be achieved with no additional Fe in the leach, but probably at a slower rate.

Fe definitely appears to have an impact on the formation of elemental sulphur, although the leach kinetics are faster, up to a stage where the molten elemental sulphur in the surface layer has inhibited migration of the oxidant to the particle surface to such an extent that it slows down the sulphide oxidation completely.

6.9.3 Discussion on temperature variations

From **Graph 46**, it is evident that the elemental S portion of the total S extracted decreases from 85% (110^{o}C) to 78% (130^{o}C) to 47% (150^{o}C), which is a clear indication that elemental S in the molten state has been oxidised to sulphate ions, more so with increasing temperature. This oxidation was only 7% more at 130^{o}C and 38% more at 150^{o}C, when compared to the test done at 110^{o}C. It is therefore proposed that, **Reactions 120 and 123** were very dominant at 130^{o}C, while **Reactions 119**, **121, 124 and 125** continued at an appreciable rate only in the two higher temperature tests. In order to oxidise the elemental sulphur to sulphate, six electrons are required, and if it is assumed that an elemental S layer is surrounding the particles, then as the oxygen and ferric ions is passing into this layer, a large proportion of the oxygen and ferric would be used for this oxidation process (**Reactions 121 and 124**), instead of oxidising the sulphide particles. Elemental S oxidation to sulphate and the sulphide residue oxidation are both competing for the same supply of oxygen and ferric ions in the higher temperature tests. The ferrous ion oxidation to ferric is also tapping into this same supply of oxygen.

This is a possible explanation of why better Cu extraction results could be achieved at 130^{o}C than in the two higher temperature tests. Also, although oxygen solubility is increasing with increasing temperature, the dissolved oxygen concentration (mg/l level) is so low, that the ferric ions (g/l) would probably be the largest contributor to sulphide oxidation.

The difference in extraction rates between 110°C and 130°C shows that once the elemental S melts, it could begin to coat particles resulting in a negative impact on extraction rates due to slower oxygen and ferric ion diffusion through this surface layer surrounding the particles. This is apparent from **Graphs 46** and **47** showing reduced rates of Ni and Cu leaching after the initial phase with increasing temperature. This would explain why the test done at 110°C has the highest total extraction and also the highest extraction rate after the initial phase. Because of the above it is proposed that at 130°C, oxygen and ferric ions will diffuse through the elemental S surface layer at a specific rate. This will then oxidise sulphide sulphur to elemental sulphur (**120** and **123**), but not elemental S to sulphate ions (**121** and **124**), because elemental S oxidation does not really occur at an appreciable rate at this temperature. The combined supply from both ferric and oxygen will only be used for sulphide sulphur oxidation to elemental S, and not for the additional oxidation of elemental S to sulphate ions, and hence the extraction at 130°C is better than at the higher temperatures.

Because reaction (**123**) takes place at a comparatively higher rate, ferric ions will be reduced and ferrous ions will be supplied back to the surrounding solution more rapidly , the Fe^{3+}/Fe^{2+} ratio and hence redox potential would be lower and change more slowly in the course of the leach as can be observed in **graphs 48–50**. It can be said hence that the sulphide oxidation by ferric ions slows down the rate of change in redox potential.

It certainly appears, therefore, that both the rate and final extent of Ni and Cu extractions are better at 110°C, possibly because elemental sulphur is not in the molten state. According to **Graph 46**, the elemental S portion of total S in the final residue is approximately 80–85% in the lower temperature tests, while only about 50% at the higher temperatures. Although the total sulphur extraction is more or less the same, the lower temperature tests contained much more elemental sulphur.

6.9.4 Discussion on oxygen partial pressure variations

After the heat up period in the 540Kpa test, 85 % Ni dissolved via the metathesis mechanism, and dissolution of hydroxides with the acid produced from ferrous precipitation. Cu extractions at the start of the acid addition period are 45% Cu at 140kPa, 53% at 340kPa and 65% at 540kPa, which illustrates the extra oxidation power of the oxygen due to higher oxygen partial pressures.

There is extra oxidation during the acid addition period, but after this period there was only reasonable extraction in the 140kPa test of 28% Cu at 140kPa, 9% at 340kPa, and 2% at 540kPa, which shows that when acid is added to the mix in the presence of Fe, coating of the particles happens due to the formation of elemental S. Referring to graph 56, this can be clearly observed in the 340kPa and 540kPa tests, where the Cu extraction comes to a virtual halt after the acid addition period.

The question could then be asked why the coating affects the tests done at 540kPa more than the test done at 140kPa. The only explanation would be that at the higher oxygen partial pressure, the ferrous oxidation to ferric is a lot quicker (**Reaction 122**), which would provide a much higher concentration of ferric ions surrounding the sulphide particles. The higher oxidation power at the particle surface generates elemental S at a much faster rate and therefore starts coating the particles more quickly. This then also strengthens the argument that when Fe is added to the mix, the formation of elemental S is promoted, possibly due to it being a quicker mechanism because of the higher concentration relative to oxygen. Dissolved oxygen will be present in mg/l amounts, while ferrous ions were added into the mix at 2 g/l. Therefore, ferric will possibly be the main oxidant at the particle surface, even though 8 moles ferric is needed to do the same as 2 moles oxygen in direct oxidation of sulphide to sulphate. Because ferric is present as the main oxidant, the formation of elemental sulphur would be promoted as discussed previously. Although ferric is the main oxidant in relation to the particle surface, oxygen remains the most important because ferrous ion regeneration cannot occur without it. When comparing results in the final residue only, ie **Graph 54**, the above rationale would then suggest significantly higher elemental sulphur in the final residue of the 540kPa test. This, however, is not the case, as the lower the oxygen partial pressure, the more elemental S is present in the final residue (**Refer to Table 38**).

At the higher oxygen partial pressure of 540kPa, the concentration of oxygen in solution will be higher, and this would speed up the rate of all reactions, which is indeed observed initially. But very quickly in the higher oxygen partial pressure tests, the elemental sulphur layer surrounding the sulphide particles builds up, leading to a slow migration rate through the surface layer and a subsequently reduced oxidation rate of the sulphide particles. It is, however, not only this that slows down the oxidation rate, but also the oxidation of elemental S in the surface layer as stated in **Reaction 121** and **124**. This combined effect, ie slow migration through the surface layer and the occurrence of **Reactions 121** and **124** in the surface layer, is using the combined oxidation power of oxygen and ferric ions to such a large extent that the oxidation of sulphide particles comes to a virtual stand-still in the higher oxygen partial pressure test. It is speculated that the size of the sulphide particle has become much smaller in relation to the volume of molten elemental S surrounding the particles that oxidation of sulphides has virtually stopped. The oxidation of elemental sulphur has now become the main reaction in this test, and until such time as this surface layer has decreased to such an extent relative to the sulphide particle, very little oxidation of sulphides will take place.

In the 340kPa and 140kPa tests the same happens from the start but at a slower rate, so that the layer of molten elemental S surrounding the particle, relative to the size of the sulphide particle, permits oxidation of the sulphide particle to continue for longer, until the ratio of surface layer to sulphide particle size has increased to such an extent that the oxidation of elemental sulphur becomes the main reaction.

The final Cu extractions do not seem to differ significantly over a 4-hour leach period, and it does not seem to have a huge impact if the test is done over a 4-hour period.

If the above theory about the oxidation of elemental S to sulphate is correct, then logically more elemental S should be present in the test done at the lowest oxygen partial pressure, simply because less oxygen is available for the oxidation to sulphate. The elemental S portion of total S is 55% (140kPa) to 49% (340kPa), and to 32% (540kPa) in the final residue, because elemental S oxidation is slower at the lower oxygen partial pressure. This is then consistent with the above theory, and the following two reactions of copper take place:

$$\mathbf{CuS + H_2SO_4 + 0.5O_2 \rightarrow S^o + CuSO_4 + H_2O} \qquad \mathbf{(127)}$$

$$\mathbf{CuS + 2O_2 \rightarrow CuSO_4} \qquad \mathbf{(128)}$$

Although both of these reactions will oxidise 1 mole of CuS, **Reaction 128** will need four times the amount of oxygen present as dissolved oxygen. The difference between 140kPa oxygen and 540kPa is virtually four times, so the copper dissolution from these two reactions should happen at much the same rate.

When comparing the effect of increasing temperature with increasing the oxygen partial pressure, it seems that increasing oxygen partial pressure would have the bigger impact on extraction of copper from sulphide. If the mechanisms used to explain under temperature and oxygen partial pressure results do apply, it should lead to the conclusion that it would be better to leach this the residue at 130°C and 540kPa oxygen partial pressure simply because the kinetics of elemental sulphur oxidation to sulphate at 130°C are a lot slower, and more oxidant would then be available for the direct oxidation of S^{2-} to SO_4^{2-}.

6.9.5 Discussion on acid concentration variations

There was more elemental S (as $\%S^0$ of S_{tot}) in the final residue of the higher acid concentration leaches, ie 46% for lower acid compared to 60% for higher acid leaches **(See Table 38)**. This is an indication that less sulphur oxidation to sulphate occurred via **Reactions 121** and **124**. This should in turn have the effect that more oxidant would be available for sulphide oxidation, and better Cu extractions would ensue as is in fact observed. This supports the theory that elemental sulphur oxidation to sulphate within the surface layer is using up oxidants before they can contribute to sulphide extraction. This is consistent with literature[21], suggesting that a thermodynamic analysis of reactions **119–125** shows that high acidity, low temperature and low oxygen partial pressure will favour reaction **120** and **123**, whereas decreasing acidity and increasing temperature and oxygen partial pressure, will shift the reaction mechanism in favour of the direct oxidation of sulphide ion to sulphate ion (**119** and **125**).

It is peculiar, however, that when comparing the lower acid concentration tests with the higher acid concentrations tests, time does not seem to be a significant factor, since running the leach for 60 minutes longer did not result in any improvement in Cu extraction.

An interesting observation is that at the lower acid concentrations (ie 15 g/l and 30 g/l acid) slightly higher Ni extractions are observed, although these are probably not statistically significant. The copper released from the oxidised sulphides will immediately be taken up to oxidise the nickel sulphides in close proximity via the metathesis reaction, but why this is affected by the acid concentration remains unclear.

Mineralogical analysis of the residue from the runs at higher acid concentrations, ie where the formation of S balls was detected, showed no difference in the composition of a cross section of the sulphur balls and the actual residue. This would indicate that the elemental S which formed merely coated a portion of solids and agglomerated into balls. It does, however, not appear as if it had an impact on copper extraction, as only a small proportion of total solids agglomerated (mass not determined). If this agglomerated mass became too big then it could not be suspended by agitation and hence it would sit at the bottom of the vessel without being oxidised any further. The prominence of S balls in the higher acid concentrations experiments is directly linked to the very high elemental S portion in the total residue; in fact it was the highest of all the tests done – except for the lower temperature tests. From this it can also be concluded that temperature has a bigger impact than acid on sulphur oxidation. There were no sulphur balls detected in the temperature variation test at 130°C and 30 g/l acid, even though the elemental sulphur portion of the total S was higher (78% vs. 60%), which shows that sulphur ball formation is highly dependant on acid concentration. This is also confirmed in the literature[27].

6.9.6 Discussion of PGM and trace element extractions

The concentrations of PGMs in solution were extremely low and to measure these accurately so close to the detection limit is difficult. There appears to be, however, some Rh and Ru dissolved in most tests, at least based on solution assays, but when using solids assays to calculate extractions, nothing is indicated. It appears as if increasing Fe levels and temperatures promote an increase in the dissolution of these elements, as well as a decrease in Rh extraction with increasing acid concentration.

Selenium extraction was generally in the range of 10–20%, but in the test done below the sulphur melting point, this increased to 50%. Tellurium extractions were generally in the range of 50–60%. Pb extraction varied between 10–30%, which is possibly due to the NaOH leach during which the mineralogy of Pb has been altered.

6.10 Proposed Mechanism

During all the tests which were performed in this study, it is clear that leaching kinetics is strongly affected by elemental sulphur as a product of sulphide oxidation when in the molten state – the melting point of elemental sulphur being 119°C according to literature.

$$S^0(s) \rightarrow S^0(l) \qquad (129)$$

In sulphide leaching, the following rate mechanisms are at work **(also see Figure 8)**.

Oxygen

1 Oxygen transfer from gas phase to solution phase.

2 Oxygen rate of migration through the surface layer (elemental S) to the sulphide particle and back to the solution surface layer interface.

3 Oxidation of the sulphide particle with two reactions extremely dependant on oxygen partial pressure and temperature

$$2S^{2-} + O_2 + 4H^+ \rightarrow 2S^0 + 2H_2O \quad (130)$$

$$S^{2-} + 2O_2 \rightarrow SO_4^{2-} \quad (131)$$

4 Oxidation of elemental S to sulphate in the surface layer

$$2S^0 + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ \quad (132)$$

5 Oxidation of elemental S to sulphate in the surrounding solution

$$2S^0 + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ \quad (133)$$

6 Oxidation of ferrous to ferric

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \quad (134)$$

Ferric

7 Ferric rate of migration through the surface layer (elemental S) to the sulphide particle and back to the solution surface layer interface.

8 Oxidation of the sulphide particle with two reactions extremely dependant on oxygen partial pressure, temperature and acid concentration

$$2Fe^{3+} + S^{2-} \rightarrow S^0 + 2Fe^{2+} \quad (135)$$

$$8Fe^{3+} + S^{2-} + 4H_2O \rightarrow 8Fe^{2+} + 8H^+ + SO_4^{2-} \quad (136)$$

9 Oxidation of elemental S to sulphate in the surface layer

$$6Fe^{3+} + S^0 + 4H_2O \rightarrow 6Fe^{2+} + 8H^+ + SO_4^{2-} \quad (137)$$

10 Oxidation of elemental S to sulphate in the surrounding solution

$$6Fe^{3+} + S^0 + 4H_2O \rightarrow 6Fe^{2+} + 8H^+ + SO_4^{2-} \quad (138)$$

At low temperatures, **reactions (130)** and **(135)** predominate and elemental S is generated, which stays solid at temperatures below the sulphur melting point, ie 119°C. At higher temperatures, **Reactions (131, 132** and **133)** and **(137** and **138)** become more and more significant. At very high temperatures (>140°C) **Reaction (136)** may also occur. At moderate temperatures > 119°C **Reaction (129)** occurs in conjunction with **(134), (130)** and **(135)**, while **(131, 132** and **133) and (137** and **138)** are not yet dominant. This results in coating of particles and retardation/passivation of further oxidation. At 130°C, passivation has occurred but reactions **(134)**, **(130) and (135)** can continue at a slower rate. With a further increase in temperature, reactions **(131, 132** and **133), (137** and **138)** and eventually **(136)** become more dominant, resulting in a higher demand for oxygen per mol metal in solution because of the increased production of sulphate. If the oxygen supply is limiting this will invariably result in a retardation of the rate of metal leaching.

The Fe tests were all done at 140°C where the oxidation to sulphate is already significant. With no Fe present, elemental S passivation does not occur, and reaction **(131)** dominates. With Fe present **(135)** and **(131)** compete, resulting in the formation of some elemental S which somewhat retards the overall reaction. The degree of retardation is a function of the sulphur layer thickness, which in turn increases with the concentration of Fe. However, with a lot of Fe present, **Reactions (137** and **138)** begin to dominate over **(135)** and hence the more efficient leaching (in terms of oxygen demand per mol metal leached) begins to counteract the retardation. Furthermore, oxygen gets consumed faster in **Reaction (134)** at high Fe concentrations than in **Reactions (131)**, **(132)** and **(133)**, which is why these become less significant.

In the tests where Fe was added, it can immediately be seen that the S_{total} extraction is dropping substantially because of the generation of elemental S, which increases substantially, with the concomitant decline in copper extraction. It is therefore proposed that in these instances **Reactions 130** and **135** are the key reactions taking place, yet **Reaction 135** would be the more dominant because of the higher Fe concentration relative to oxygen, mineral oxidation proceeds more rapidly by Fe than by oxygen directly, and ferrous is more easily oxidised to ferric by oxygen due to the concentration effect in the surrounding surface layer. The S^o forms from the S^{2-} oxidation in the immediate vicinity of the particle, resulting in the formation of a layer around the sulphide particle, mostly containing S^o. The diffusion rate through this layer becomes slower due to two mechanisms:

(a) The viscosity increase and subsequent slower diffusion rates of ferric and oxygen acting as electron carriers for the oxidation of S^{2-} to take place.

(b) The ferric and oxygen which upon entering the surface layer enter into a chemical reaction with the S^o according to **Reaction 132** and **137**, which oxidises S^o to SO_4^{2-}, and uses the combined oxidative power for this, rather than oxidising the sulphide minerals, thereby inhibiting Cu extraction. This also has a negative impact on acid and ferrous ions generated in this surface layer, causing a high acid concentration surrounding the sulphide particle, which in the presence of Fe will promote the formation of S^o. The higher ferrous concentration in the surface layer ensuing from this, will grab any oxygen trying to diffuse to the particle surface and form Ferric ions according to **Reaction 134**.

The particle size relative to the surface layer thickness will decrease, if the rate of oxidation of the sulphide particle is quicker than the rate of oxidation of the S^o to SO_4^{2-}. This can only happen if the diffusion rate through the surface layer is quicker than the chemical oxidation rate of S^o to SO_4^{2-} . This would certainly happen in the early stages of the leach.

The chances therefore of any direct oxidation of sulphide to sulphate **(Reactions 131** and **136)** are diminished due to the above effects and mechanisms described.

Electrons are transferred to oxygen and ferric ions. It is observed that the S^o in the residue increases as the Fe concentration increases from 0 to 2 g/l Fe. It would then be expected that Cu extraction would follow the same trend, but it does not, as at a higher Fe concentration, the rate of migration through the surface layer to the particle surface increases and therefore faster S^o to SO_4^{2-} oxidation can take place. Increasing the Fe concentration even more, the Cu extraction rate increases slightly, but the rate of S^o generation is now exceeded by the rate of S^o to SO_4^{2-} oxidation, which is why the S_{total} extraction increases.

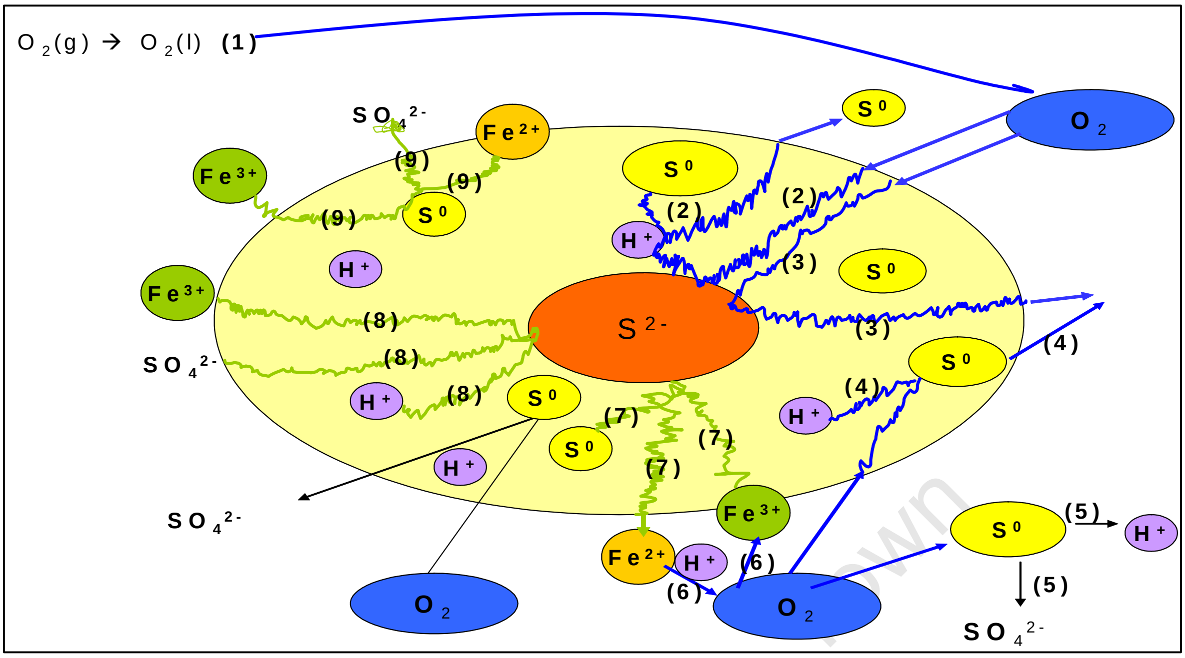


Figure 8: Figure of proposed mechanism

6.11 Conclusions

Refer for all results to **Table 38** in this section

In the oxidation of sulphides and the subsequent release of copper and nickel, the following were the major findings:

1 Temperature has the most significant impact in the type of sulphur prevalent in the final residue. When operating below 130°C, the kinetics of elemental sulphur oxidation to sulphate are very slow, resulting in a high elemental sulphur portion in the total reaction mixture.

2 Whether operating below or above the sulphur melting point of 119°C has a marked impact on process performance, in that when elemental sulphur is not in the molten stage, it does not impact on the oxidant (ie oxygen and Fe) migration to and from the sulphide particles, which results in much better extractions for the same oxidant concentrations, oxygen partial pressure and acid concentrations. The highest copper extractions were achieved with leaching at 110°C. Although the rate of leaching is reduced at the lower temperatures, the rate of leaching above the sulphur melting

point, ie when there is a surrounding molten sulphur layer around the particle, the rate of leaching is reduced to that of diffusion and any gain made by operating at the higher temperatures is offset by the formation of the sulphur layer. Although this leach did not result in the highest mass loss overall due to the elemental sulphur not being oxidised, the best sulphide extraction was achieved. If this elemental sulphur can be dissolved via a subsequent NaOH leach, even without oxygen, the ensuing mass loss would be the best by some margin.

3 Operating above the melting point of sulphur, but below 130°C, would also achieve very good sulphide extractions, but with less sulphur oxidation. The elemental sulphur surface layer surrounding the particles would restrict oxidant flow to and from the sulphide particles.

4 If the temperature is increased to 140–150°C, elemental sulphur oxidation to sulphate become much more prevalent, resulting in a large proportion of the oxidant entering the elemental sulphur surface layer surrounding the particles to be used for sulphur oxidation, which has no benefit in terms of sulphide oxidation. It can only have a benefit when the rate of the elemental sulphur oxidation to sulphate in the surface layer is higher than the rate of sulphide oxidation to elemental sulphur. This would result in the surface layer decreasing in size relative to the sulphide particle, thereby decreasing the distance of the path of migration of oxidant to the sulphide particle, ie the oxidant will reach the sulphide particle more quickly.

5 Ferric concentration in the leach also has a marked impact on sulphide oxidation. If no Fe is present in the leach, the highest sulphur extraction resulted by far. The reason is that sulphide oxidation directly to sulphate is a lot more significant, ie very little elemental sulphur forms as a product of the reaction mechanism, and therefore a much thinner surface layer in relation to sulphide particle size is maintained, decreasing the distance of the path of migration of oxidant to sulphide particle. Also, the only oxidant operating in the leach is oxygen and it is not consumed by ferrous oxidation to ferric, nor by elemental sulphur oxidation to sulphate.

6 On the addition of Fe to the leach, it is evident from the test work that the product of the leach reactions immediately indicates a large presence of elemental sulphur. It can

therefore be concluded that although Fe is an additional oxidant, the production of elemental sulphur and the subsequent coating of the particles with an elemental sulphur surface layer restrict the flow of oxidant to the sulphide mineral surface by increasing the length of oxidant path. The oxidants, ie oxygen and Fe, are also consumed by the oxidation of elemental sulphur to sulphate on this path, without being of benefit in the oxidation of the sulphide minerals. The oxygen as oxidant will also be consumed by the regeneration of ferrous ions to ferric ions.

7 Because oxygen concentration in solution (dissolves only to mg/l) is small, compared to Fe concentration (g/l), and ferrous is easily oxidised to ferric in solution, it can be concluded that ferric will act as the main oxidant in the tests performed. The by-product of elemental sulphur oxidation to sulphate is acid, which will result in high acid concentrations in the vicinity of the sulphide particles, which in turn promotes the formation of proportionally more elemental sulphur. This is confirmed in both the literature and this testwork. The only time ferric as oxidant is beneficial to sulphide leaching, is when a large excess of this oxidant is present, enough so that the rate of elemental sulphur production would be slower, or at least the same as, the rate of elemental sulphur oxidation to sulphate, thereby decreasing or keeping the surface layer size in relation to the particle size reasonable.

8 Increasing the oxygen partial pressure in the presence of Fe in the leach results in a much faster oxidation of elemental sulphur to sulphate. However, this would only enhance the rate of sulphide oxidation if the mechanism explained in (**7**) above is true. It would, however, ensure a lower overall residue mass due to elemental sulphur oxidation to sulphate.

9 Increasing acid concentration in the range tested does not appear to have a negative impact on sulphide extraction to any great extent, when keeping all the other parameters and oxidant concentrations constant, but it definitely promotes the formation of elemental sulphur as a product of the reactions.

Table 38: Summary of key parameters and major BM extractions on final residues

SUMMARY OF THE KEY PARAMETERS OF THE FINAL SAMPLE RESULTS

Variation	Condition	%Ni Extr	% Cu Extr.	% Mass Loss	$\%S_{tot}$ Extr.	% S^o of S_{tot}	% S^o of total solids	$\%S_{tot}$ assay	Leach Time	Total BM + S	BM : S ratio
RES A		61	58	52	42	37	16	45	260	93	0.54
RES B		28	11	9	11	66	37	56	144	94	0.35
NaOH Res		87	73	64	33	49	23	47	240	94	0.50
Ferrous (g/l)	0	100	83	82	75	23	8	34	285	88	0.78
	1	88	69	70	43	33	16	48	240		
	2	88	73	64	33	49	23	47	240	94	0.5
	3	88	76	73	57	33	13	41	240	93	0.66
TEMP	110	92	93	76	33	85	59	69	302	88	0.13
	130	87	89	73	32	78	49	63	295	90	0.21
	140	87	73	64	33	49	23	47	240	94	0.50
	150	87	73	64	35	47	22	47	240	95	0.52
pO_2	140	74	78	68	39	55	27	49	305	93	0.46
	340	87	73	64	33	49	23	47	240	94	0.50
	540	97	81	78	66	32	13	39	300	91	0.67
Acid(g/l)	15	86	74	64	39	46	20	44	300	90	0.53
	30	87	73	64	33	49	23	47	240	94	0.50
	50	80	76	63	18	63	35	56	240	98	0.37
	60	80	77	67	27	60	33	55	300	99	0.40
Agitation rpm	30	85	81	71	40	60	31	52	300	94	0.40
	40	87	73	64	33	48	23	47	240	94	0.50

	50	79	73	64	28	53	26	50	245	97	0.47
	60	78	77	69	40	50	25	49	300	98	0.49

Table 39: Summary of key parameters and major Trace and PGM extractions on final residues

SUMMARY OF THE KEY PARAMETERS OF THE FINAL SAMPLE RESULTS

Variation	Condition	%Se Extr	% Te Extr.	%Stot Extr.	% So of Stot	Rh mg/l	Ru mg/l	Pb mg/l	Sb mg/l	Leach Time
RES A		**22**	**47**	**42**	**37**	**<0.1**	**0.4**			**260**
RES B		**2**	**25**	**11**	**66**	**0.1**	**0.4**			**144**
NaOH Res		**22**	**52**	**33**	**49**	**0.1**	**0.7**			**240**
Ferrous (g/l)	0	50	65	75	23	<0.1	0.3	0.6	0.5	285
	1	-	-	43	33	0.1	0.8	-	-	240
	2	23	51	33	49	0.1	0.7	0.9	0.4	240
	3	31	65	57	33	0.2	0.7	0.6	0.3	240
TEMP	110	50	50 – 60%	33	85	<0.1	0.5	0.6	0.4	302
	130	26		32	78	<0.1	0.5	0.7	0.3	295
	140	22		33	49	0.1	0.7	0.9	0.4	240
	150	22		35	47	0.2	0.7	0.6	0.3	240
pO2	140	28	56	39	55	-	-	-	-	305
	340	22	52	33	49	0.1	0.7	0.9	0.4	240
	540	35	72	66	32	0.2	0.6	0.6	0.3	300
Acid(g/l)	15	20	60	39	46	0.2	0.7	0.7	0.1	300
	30	21	50	33	49	0.1	0.7	0.9	0.4	240
	50	10	45	18	63	0.1	0.7	1.2	0.6	240

	60	20	52	27	60	<0.1	0.6	0.6	0.6	300
Agitation rpm	30	20–30%	50 – 60%	40	60	<0.1	0.6	0.6	0.3	300
	40			33	48	0.1	0.7	0.9	0.4	240
	50			28	53	0.1	0.6	0.4	0.3	245
	60			40	50	0.2	0.7	0.7	0.3	300

6.12 Development of Process Scenarios

6.12.1 Operating above the S^o melting point

Scenario 1

According to **Table 38**, the best would be to limit S^o generation when operating above the melting point of S^o, since it is the biggest factor limiting the extraction of Cu and Nickel with this residue. The only way this can be achieved is by not adding Fe to the leach and limiting the addition of acid to the mix. Acid is unnecessary for Cu extraction if no Fe is added, it is only to prevent the precipitation of copper as antlerite (basic Cu sulphate). It would make sense, therefore, to suggest that the leach should progress for some time before starting acid addition in order to dissolve the antlerite that may have precipitated in the meantime. It would then also make sense to operate the leach at just above the S^o melting point temperature, ie 120–130°C, simply because the test work shows that the kinetics of S^o to SO_4^{2-} oxidation are very slow at this temperature, while a higher oxidant concentration promotes S^{2-} oxidation. The oxidant would then not be consumed unnecessarily by the oxidation of S^o to SO_4^{2-}, since the leach will only oxidise the sulphides to elemental sulphur. Increasing the oxygen partial pressure would also help in order to compensate for the lower oxygen solubility at the lower temperature. The only aspect which could limit this scenario would be a declining diffusion rate of the oxidant with time, as the elemental S layer around the particle will become larger because there is very little S^o to SO_4^{2-} oxidation and this could possibly prevent complete extraction within a reasonable time. This would probably be a function of initial particle size distribution and progression of the leach rate. If favourable, then the leach might be complete before passivation occurs.

A high agitation rate will not improve extraction because the test work has shown that at the slower agitation rates, less S^o to SO_4^{2-} oxidation takes place, so less oxidant would be wasted on S^o to SO_4^{2-} oxidation.

A further benefit of this scenario for leaching would be that the PGM dissolution would be limited as well. It is also likely to result in the highest Se and Te extractions, as proven in the test work.

PROPOSED LEACH CONDITIONS AND PREDICTED EXTRACTIONS			
Temperature	130°C	Cu	89%
Ferrous addition	0g/l	Ni	100%
pO2	540kPa	S → SO_4^{2-}	80%
Agitation	200rpm	Stochiometric S → S^o	15%
Acid	15g/l	Se/Te	35/70%
Mass Loss from NaOH leach	44%		
Mass Loss from H_2SO_4 leach	87%		
Mass Loss from H_2SO_4 leach after removing S^o fraction	90%		

Table 40: Proposed leach conditions and extractions Scenario 1

6.12.2 Operating below the S^o the melting point

High Fe addition to leach

Scenario 2

This would mean operating at a low temperature, possibly at 110°C, because the elemental S which forms does not melt and hence does not form an elemental S surface layer around the particle, which limits the access of oxidant to the particle surface. Also, the effect of S^o to SO_4^{2-} oxidation will be much less of a factor, as the rate of this reaction is very slow at this temperature. In this case, the oxidant can be increased to achieve maximum rates because the S^o formed will not inhibit leaching of Cu and Ni. Therefore, ferrous ion addition can be maximised and the oxygen partial pressure can be increased to maximum, thereby supplying the leach with a maximum amount of oxidant. Only enough acid should be available in order to keep all the Fe and Cu in solution, and to supply enough acid for ferrous to ferric oxidation. Higher agitation rates would be preferable in this case as the development of a surface layer is much more limited and better agitation should help to minimise this further. PGM extraction should not be significant, while Se and Te extractions will be at maximum rates, as proven with the test work

PROPOSED LEACH CONDITIONS AND PREDICTED EXTRACTIONS			
Temperature	110°C	Cu	97%(+4% from 110°C)
Ferrous addition	3g/l	Ni	98%(+1% from 540kPa)
pO2	540kPa or higher	S → SO_4^{2-}	35%
Agitation	440rpm	Stochiometric S → S^o	60%
Acid	15g/l	Se/Te	50/65%
Mass Loss from NaOH leach	44%		
Mass Loss from H_2SO_4 leach	79%		
Mass Loss from H_2SO_4 leach after removing S^o fraction	97%		

Table 41: Proposed leach conditions and extractions Scenario 2

The primary question to be asked in the beginning of a test work campaign is obviously at what rate sulphur oxidation can occur, and if this important at all. In this instance, the aim is both to extract as much of the base metals as possible and to limit the extraction of PGMs – sulphur oxidation to sulphate is not important. By operating at a temperature above the melting point of sulphur, it is shown with this residue that the surface layer surrounding the particles will slow down the extraction of base metals. Therefore a low temperature leach would be better, thereby limiting sulphur oxidation and maximising the use of oxidant for only base metal oxidation. Thus, better extraction rates should be possible with scenario 2.

All of the values above, although calculated, remain predicted and need to be tested to ascertain the actual extraction values. Also, if operating below the sulphur melting point, consideration could be given to direct leaching of the CPL residue without an intermediate NaOH leach in order to clean the residue from any elemental sulphur which would inhibit extraction, as the elemental sulphur present in the residue would not be molten.

SECTION 7

OVERALL ASSESSMENT OF A CAUSTIC LEACH AND A SULPHURIC ACID LEACH IN TREATING THIS RESIDUE

The CPL residue from the new BMR process contains too much elemental sulphur, which inhibits complete extraction of residual Cu and Ni values in the CPL process. The elemental sulphur leads to the formation of an agglomerated mass of residue, which gathers in the bottom of the autoclave. A direct re-leach of this residue using sulphuric acid as lixiviant would hence be equally inhibited by this sulphur. It is therefore proposed that the residue is treated in an oxidative NaOH leach, in order to dissolve all the elemental sulphur, before pressure leaching. As determined by the test work presented in section 4, this can be done successfully by leaching for a 20 minute period in hot caustic solution at 80°C.

Although the test work was done on residue gathered from the A period during the new BMR process test work (no Fe added during the CPL leach), all the results can be extrapolated to material from the B period (where Fe was added to the CPL leach), which is the likely new process condition. The main difference in the residues is that Cu concentrations were lower, Fe concentrations were higher and elemental S concentration was substantially higher in the B period residue.

The sole purpose of the NaOH leach is to remove any elemental S, which was successfully demonstrated in the test work. During a 20 minute NaOH leach, the extraction of elemental sulphur will be more or less complete, while copper extractions are likely to be minimal (2%), and no nickel nor iron extraction were observed. Some Se and Te will also be extracted. Pb is converted to a solid species which will partially dissolve in the subsequent sulphuric acid leach.

The residue from this NaOH leach is then to be treated further by a sulphuric acid pressure leach. Employing Scenario 2 as outlined in the preceding chapter, for this, 97–98% of the Cu and Ni are predicted to leach under conditions of low temperature and high oxidant addition within 4 – 6 hrs of leaching time. This will lead to a sulphur oxidation of 40% in the sulphate form, while 60% will remain as elemental S in the residue. As sulphur is not desirable for further processes to recover PGMs from the residue, another 20 minute caustic leach step would be required in order to remove this elemental S portion as well.

If doing the leach as described in Scenario 1, then 89% Cu and 100% Ni would leach. This will lead to sulphur oxidation of 80% in the sulphate form, and 10–15% of the sulphur will remain in an elemental S form in the residue. The benefit of this scenario is an additional NaOH leach step would not be needed, but a significantly lower mass loss will ensue. According to a mass balance (Table 44) that was done to compare the two scenarios, the following will result:

	Overall % Mass Loss	Kg final mass/t CPL starting residue
Scenario 1	94	60kg
Scenario 2	98	20kg

Table 42: Comparing two scenarios

Selenium extractions were 57–73%, and tellurium extractions 19–25% during the continuous NaOH leach tests and similar results are expected here. The speciation of the selenium and tellurium was not analysed, but tellurium is not really soluble at these caustic conditions, because most of the tellurium would precipitate as tellurate. If the leach was done for a shorter period (20 minutes) possibly much better Te extractions could be achieved in solution as the tellurite species.

The sulphuric acid pressure leach under the conditions described would extract in the order of 50% selenium and 65% tellurium in the sulphuric acid leach. This would result in a total Se extraction of 78% and 68% Te respectively in both leaches combined. This solution would then be sent to the main Cu feed stream, on its way to the Se and Te removal step. The selenium/ tellurium in this stream would be so little overall, that in a 50 m^3/hr stream, it would increase the Se concentration by 8 mg/l relative to current levels, which is likely to be removed in the existing Se removal process into which the Cu feed stream flows.

PGMs were extracted, mostly in the NaOH leach, and this had been calculated according to solids assays, but no PGMs could be detected in the solution assays. Therefore the estimated extractions could well be incorrect. In the sulphuric acid leach under the conditions proposed, only Ru extraction would be in the order of 15%. It must however be stressed that PGM results were largely inconclusive and the indicated results must be treated with some caution.

Pb was the major trace element impurity which could be detected and it was extracted to 56% in the NaOH leach. Another 16% dissolution occurred in the sulphuric acid leach, probably because the Pb mineralogy was altered during the caustic leach. This is beneficial if the aim is to blend the final residue from this process with the PMR feed material. In the abbreviated mass balance in Table 44, extractions of other trace element impurities were as indicated in Table 43.

	NaOH leach Extraction	**H_2SO_4Leach Extraction**	**Total Extraction**
As	44%	-	44%
Sn	39%	-	39%
Sb	24%	13%	34%

Table 43: Extractions of NaOH leach and Sulphuric acid leach scenario 2

The objective of identifying and then testing a possible hydrometallurgical process route for treatment of the CPL residue had been achieved with reasonable success. A better understanding of the mechanisms and possible conditions for treating this residue has been developed. Nonetheless, continuation of this work is required in order to finalise and test a complete flowsheet for the treatment of the CPL residue.

The following is work which is proposed for additional test work:

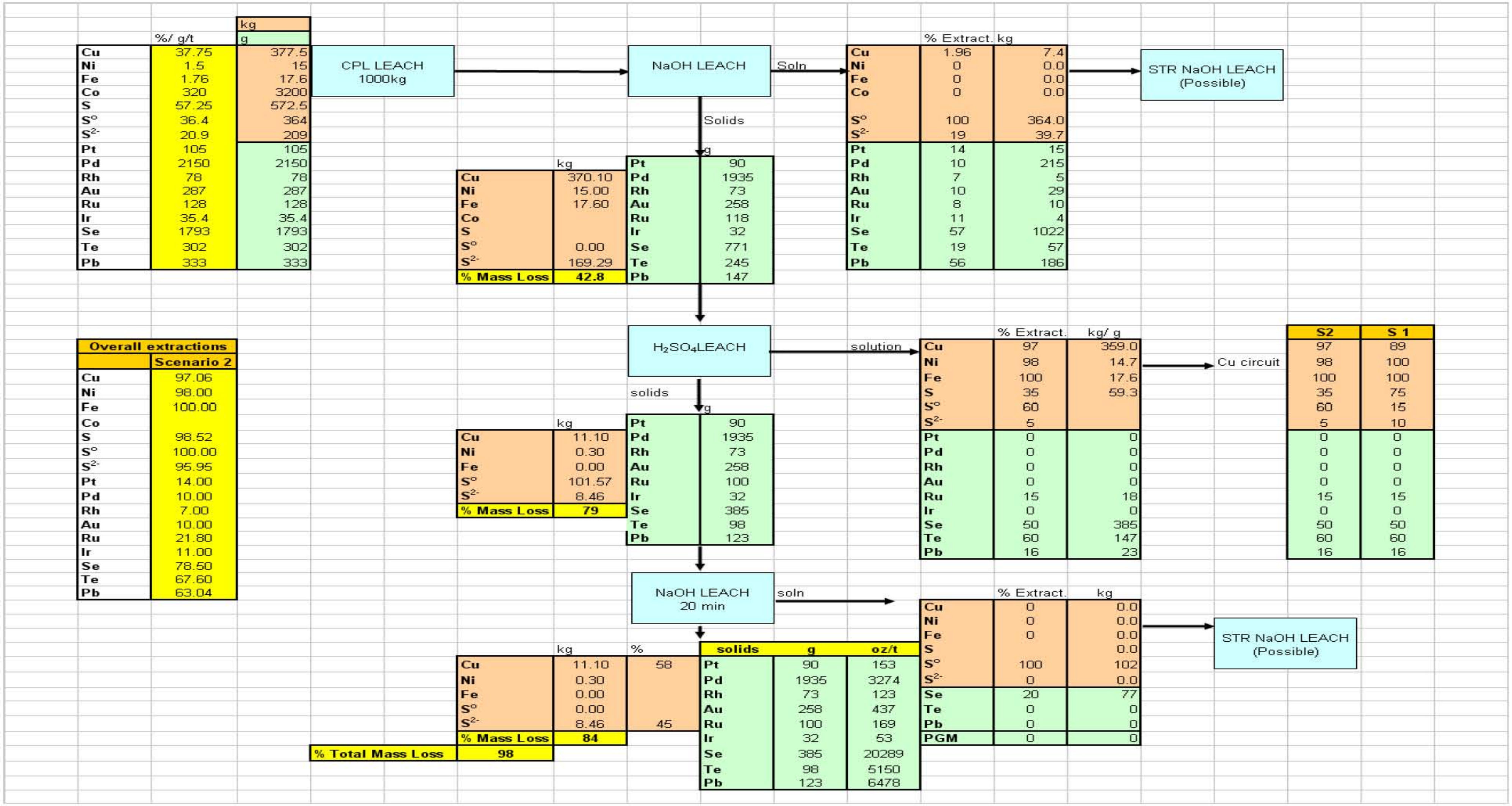
1. Testing the actual CPL residue with a direct sulphuric acid leach at 110^{o}C, without treating the residue in a NaOH leach first.
2. Testing the two scenarios proposed and providing a confirmed mass balance.
3. Treating the residue from (1), with a NaOH leach after a sulphuric acid leach.

4 Attempting to understand the difference in amorphous and orthorhombic sulphur better.

5 Developing a leach to free the residue obtained during this test work from any silver.

6 Testing whether complete conversion of sulphides during a long NaOH leach (potentially under pressure) can be achieved, followed by a simple atmospheric acid wash to dissolve all soluble Cu and Ni; it might be simpler and work just as well.

Table 44: Abbreviated mass distribution of elements in scenario 2



	%/ g/t	kg g
Cu	37.75	377.5
Ni	1.5	15
Fe	1.76	17.6
Co	320	3200
S	57.25	572.5
S°	36.4	364
S^{2-}	20.9	209
Pt	105	105
Pd	2150	2150
Rh	78	78
Au	287	287
Ru	128	128
Ir	35.4	35.4
Se	1793	1793
Te	302	302
Pb	333	333

CPL LEACH 1000kg → NaOH LEACH

NaOH LEACH – Soln:

	% Extract.	kg
Cu	1.96	7.4
Ni	0	0.0
Fe	0	0.0
Co	0	0.0
S°	100	364.0
S^{2-}	19	39.7
Pt	14	15
Pd	10	215
Rh	7	5
Au	10	29
Ru	8	10
Ir	11	4
Se	57	1022
Te	19	57
Pb	56	186

→ STR NaOH LEACH (Possible)

NaOH LEACH – Solids:

	kg
Cu	370.10
Ni	15.00
Fe	17.60
Co	
S	
S°	0.00
S^{2-}	169.29
% Mass Loss	**42.8**

	g
Pt	90
Pd	1935
Rh	73
Au	258
Ru	118
Ir	32
Se	771
Te	245
Pb	147

Overall extractions	
	Scenario 2
Cu	97.06
Ni	98.00
Fe	100.00
Co	
S	98.52
S°	100.00
S^{2-}	95.95
Pt	14.00
Pd	10.00
Rh	7.00
Au	10.00
Ru	21.80
Ir	11.00
Se	78.50
Te	67.60
Pb	63.04

H_2SO_4LEACH – solution:

	% Extract.	kg/ g
Cu	97	359.0
Ni	98	14.7
Fe	100	17.6
S	35	59.3
S°	60	
S^{2-}	5	
Pt	0	0
Pd	0	0
Rh	0	0
Au	0	0
Ru	15	18
Ir	0	0
Se	50	385
Te	60	147
Pb	16	23

→ Cu circuit

S2	**S 1**
97	89
98	100
100	100
35	75
60	15
5	10
0	0
0	0
0	0
0	0
15	15
0	0
50	50
60	60
16	16

H_2SO_4LEACH – solids:

	kg
Cu	11.10
Ni	0.30
Fe	0.00
S°	101.57
S^{2-}	8.46
% Mass Loss	**79**

	g
Pt	90
Pd	1935
Rh	73
Au	258
Ru	100
Ir	32
Se	385
Te	98
Pb	123

NaOH LEACH 20 min – soln:

	% Extract.	kg
Cu	0	0.0
Ni	0	0.0
Fe	0	0.0
S		0.0
S°	100	102
S^{2-}	0	0.0
Se	20	77
Te	0	0
Pb	0	0
PGM	0	0

→ STR NaOH LEACH (Possible)

NaOH LEACH 20 min – solids:

	kg	%
Cu	11.10	58
Ni	0.30	
Fe	0.00	
S°	0.00	
S^{2-}	8.46	45
% Mass Loss	**84**	
% Total Mass Loss	**98**	

solids	**g**	**oz/t**
Pt	90	153
Pd	1935	3274
Rh	73	123
Au	258	437
Ru	100	169
Ir	32	53
Se	385	20289
Te	98	5150
Pb	123	6478

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APPENDICES

Appendix I

Table 45: NaOH Batch leach extraction results

Solids extraction results													
Time													
	Time(min)	**% S_{tot}**	**%Cu**	**%Ni**	**%Fe**	**%SiO2**	**%Se**	**%Te**	**%Pb**	**%As**	**%Mass Loss**	**%S^{2-}**	**%S^0**
T3	20	82.6	13.6	20.4	2.0	75.7	80.4	52.7	100.0	68.9	68.0	25.3	101
T5	30	77.0	5.1	6.9	2.9	71.7	75.8	21.3	100.0	64.8	49.9	16.0	97
T4	40	81.4	18.3	23.9	17.2	22.2	99.6	26.4	100.0	66.5	55.8	29.6	98
T2	60	80.3	-2.7	-0.4	-9.0						64.4	9.1	103
Temperature													
	Temp	**% Stot**	**%Cu**	**%Ni**	**%Fe**	**%SiO2**	**%Se**	**%Te**	**%Pb**	**%As**	**%Mass Loss**	**%S^{2-}**	**%S^0**
T6	25	8.0	1.9	2.5	-9.7	41.8	17.6	14.1	100.0	44.9	7.6	12.1	7
T7	50	22.6	-0.7	-3.6	-6.1	42.8	11.4	0.0	100.0	40.4	15.1	8.5	27
T5	80	77.0	5.1	6.9	2.9	71.7	75.8	21.3	100.0	64.8	49.9	16.0	97
Solids loading													
	g/l Solids	**% Stot**	**%Cu**	**%Ni**	**%Fe**	**%SiO2**	**%Se**	**%Te**	**%Pb**	**%As**	**%Mass Loss**	**%S^{2-}**	**%S^0**
T2	50	80.3	-2.7	-0.4	-9.0						64.4	9.1	103
T1	100	73.2									49.0	0.0	105
T8	200	42.7	11.6	9.9	9.2	57.4	97.3	28.9	100.0	54.4	36.8	20.2	50
Solution extraction results													
Time													
	Time(min)	**% S_{tot}**	**%Cu**	**%Ni**	**%Fe**	**%SiO2**	**%Se**	**%Te**	**%Pb**	**%As**	**%Mass Loss**	**%S^{2-}**	**%S^0**
T3	20	54.8	0.0	0.1	0.8		96.5	64.2	0.5	92.3	68.0	80.0	15.7
T5	**30**	60.9	0.1	0.1	1.0		70.3	26.7	1.0	76.2	49.9		12.5
T4	40	61.3	1.1	0.0	0.4		98.9	54.4	0.7	84.6	55.8		50.1
T2	60	56.0	0.0	0.1	0.7		82.1	51.67	0.50	94.62	64.4		
Temperature													
	Temp	**% Stot**	**%Cu**	**%Ni**	**%Fe**	**%SiO2**	**%Se**	**%Te**	**%Pb**	**%As**	**%Mass Loss**		
T6	25	94.5	2.6	0.1	0.6	0.0	2.5	1.9	8.5	47.1	7.6		
T7	50	89.2	0.1	0.1	0.5	0.0	13.6	5.3	3.7	58.2	15.1		
T5	**80**	60.9	0.1	0.1	1.0	0.0	70.3	26.7	1.0	76.2	49.9		
Solids loading													
	g/l Solids	**% Stot**	**%Cu**	**%Ni**	**%Fe**	**%SiO2**	**%Se**	**%Te**	**%Pb**	**%As**	**%Mass Loss**		
T2	25	56.0	0.0	0.1	0.7		82.1	51.7	0.5	94.6	64.4		
T1	50	70.0	0.0	0.1	0.6						49.0		
T8	**200**	79.5	0.3	0.0	0.2		3.5	33.5	0.4	47.8	36.8		

Table 46: NaOH batch leach test conditions

Test conditions								
Run	Conditions		Initial		Volumes		Final	
Number	Time (mins)	Temp (oC)	g solids	g/l solids	Start volume (ml)	Total Volume (ml)	Mass (g)	%mass loss
1	60	50	10	100	100	200	5.1	49.0
2	60	80	25	50	500	600	8.9	64.4
3	20	80	25	50	500	600	8	68.0
4	40	80	25	50	500	400	11.04	55.84
5	30	80	25	50	500	600	12.53	49.88
6	30	25	25	50	500	680	23.09	7.64
7	30	50	25	50	500	630	21.22	15.12
8	60	80	100	200	500	700	63.2	36.8

Table 47: NaOH batch leach test accountabilities

Accountabilities								
Run Number	**Copper Account**	**Nickel Account**	**Fe Account**	**SiO2 Account**	**Se Account**	**Te Account**	**Pb Account**	**As Account**
1	142.6	135.4	156.8					0.0
2	102.7	100.4	109.7					
3	86.4	79.7	98.8	24.3	116.1	111.5	0.5	123.4
4	82.8	76.2	83.2	77.8	99.2	128.0	0.7	118.2
5	95.0	93.2	98.1	28.3	94.4	105.3	1.0	111.3
6	100.7	97.5	110.2	58.2	84.9	87.8	8.5	102.1
7	100.8	103.7	106.6	57.2	102.1	120.8	3.7	117.7
8	88.7	90.1	91.0	42.6	6.3	104.6	0.5	93.4

Table 48: NaOH batch leach assay results

Run		Assay results									
Number		Na2SO4 (g/l)	Ni (%/mg/l)	Cu (%/mg/l)	Fe (%/mg/l)	S (%)	Si (%)	Se (mg/l & %)	Te (mg/l & %)	Pb (mg/l & %)	As (mg/l & %)
1	Solution	41.89	3.7	0.4	4.6						
	Solids		33.7	31.6	4.9	33.0					
2	Solution	51.1	3.6	0.4	4.6			55	3.1	0.1	4.1
	Solids		35.8	32.6	4.9	34.8					
3	Solution	52.5	3.8	0.4	5.1			64	3.85	0.1	4
	Solids		31.6	30.5	4.9	34.1	0.35	0.0976	0.0213	0.00001	0.0101
4	Solution	67.5	3.8	80.5	3.5			99	4.9	0.2	5.5
	Solids		21.9	20.9	3	26.5	0.81	0.0013	0.024	0.00001	0.0079
	Initial solids		25.3	23.6	3.5	62.9	0.46	1595	144	480	104
5	Solution	45.4	3.9	3.4	6.8			47	1.6	0.2	3.3
	Solids		23.6	21.4	3.1	28.8	0.26	0.0769	0.0226	0.00001	0.0073
6	Solution	5.6	3.1	110	3.3			1	0.1	1.5	1.8
	Solids		13.4	12	1.9	62.6	0.29	0.1423	0.0134	0.00001	0.0062
7	Solution	12	6.6	5.4	3.3			9	0.3	0.7	2.4
	Solids		15.5	13.4	2	57.3	0.31	0.1664	0.0196	0.00001	0.0073
8	Solution	81.7	7.6	54.7	4			8	6.9	0.3	7.1
	Solids		18.1	15.8	2.3	57	0.31	0.0069	0.0162	0.00001	0.0075

Appendix II

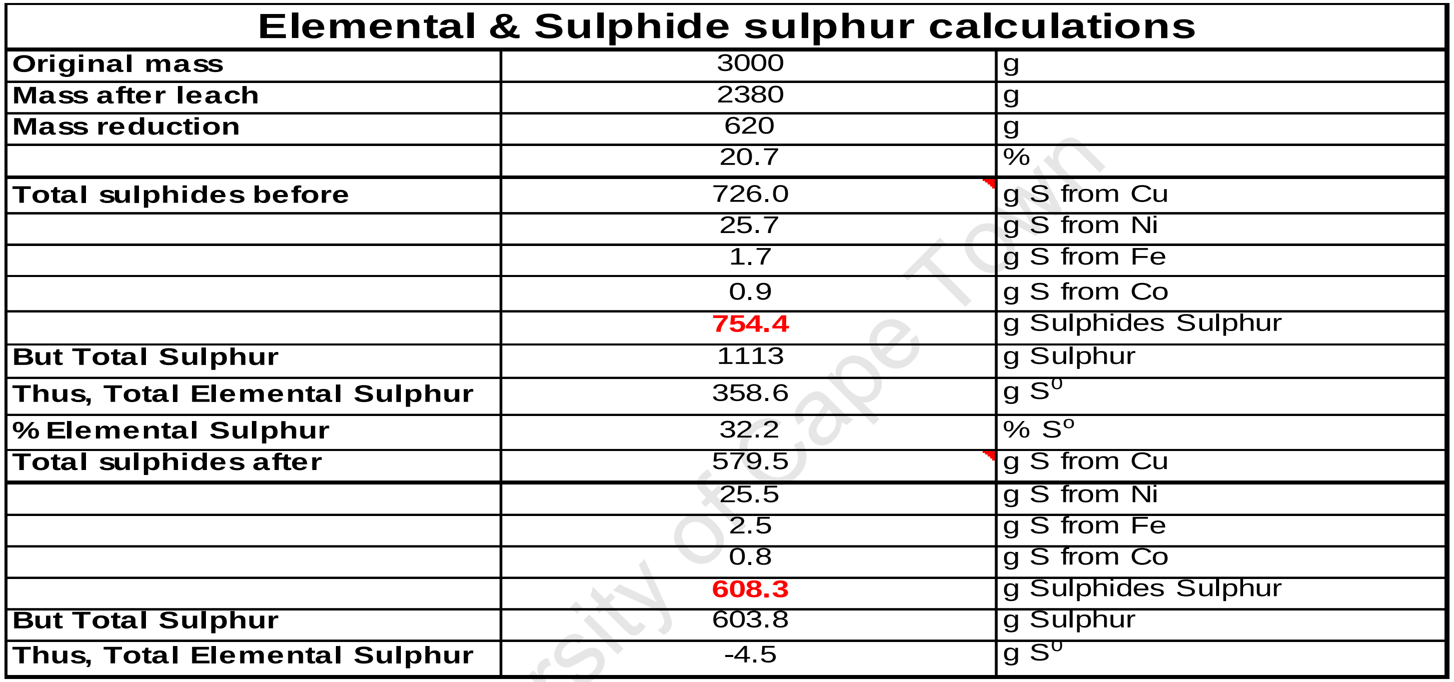
Table 49: 1^{st} NaOH continuous leach extraction results

FIRST CAUSTIC LEACH					
RESULTS	*Head solids assay*	*Tail solids assay*	*Solution assays*	*% Extraction*	*% Extraction*
	%/ g/t	*%/ g/t*	*mg/l*	*(Solution sample)*	*(Solid sample)*
Cu %	53.29	61.09	190	1.96	8.3
Ni %	1.57	1.96	<0.1	0	-1.4
Fe %	0.1	0.18	<0.1	0	-44.0
Co	580	630	<0.1	0	13.1
S %	37.1	25.37	-	36.0	45.3
Pt	45.2	48.4	-	-	14.3
Pd	819	918	-	-	10.3
Rh	42.2	49.3	-	-	6.5
Au	108	122	-	-	9.6
Ru	47	53.8	-	-	8.4
Ir	14.9	16.5	-	-	11.4
Se	1610	946	16.60	57	52.99
Te	170	173	0.41	13	18.6
Pb	118	65.9	1.72	80	55.3
As	115	81.1	0.30	14	43.6
Sn	58.3	44.7	0.42	40	38.7
Na2SO4	-	-	10780	10780	-

Table 50: 2nd NaOH continuous leach extraction results

Second Caustic leach																	
	Residue A	NaOH leach	Reactor 1	Reactor 2	Reactor 3	Reactor 1 solution			Reactor 2 solution			Reactor 3 solution			Final		
		Residue	Solid	Solid	Solids	Solutio	% Extraction	% Extraction	Solutio	% Extractio	% Extractio	Solutio	% Extractio	% Extractio	Solutio	% Extractio	% Extractio
						mg/	Solution sampl	Solid sampl	mg	Solution sampl	Solid sampl	mg	Solution sampl	Solid sampl	mg	Solution samp	Solid samp
Cu	53.29	61.09	.	.	.	0.0	0.		15	1.		16	1.		18	1	9
Ni	1.57	1.96	.	.	.	0.0	0.			0.			0.				1
Fe	0.1	0.18	.	.	.												-42
Co	580	630	.	.	.												13
S	37.1	25.37	29.5	27.4	26.3		27.	36.		24.	41.		28.	43.		27	45
Pt	45.2	48.4	48	51	48	0.0	0.0	15.7	0.0	0.0	10.4	0.0	0.0	15.7			15.
Pd	819	918	847	908	948	0.0	0.0	17.9	0.0	0.0	12.0	0.0	0.0	8.1			11.
Rh	42.2	49.3	29	3	3	0.0	0.0	45.4	0.0	0.0	43.6	0.0	0.0	43.6			7.
Au	108	122	11	117	12			19.2			14.0			10.3			10.
Ru	47	53.8	52	52	55	0.0	0.0	12.2	0.0	0.0	12.2	0.0	0.0	7.1			9.1
Ir	14.9	16.5	18	18	18	0.0	0.0	4.1	0.0	0.0	4.1	0.0	0.0	4.1			12.1
Se	1610	946	.	.	.	19.6	40.6	53.3	29.4	61.0	53.3	34.7	71.9	53.3	32.7	67.8	53.3
Te	170	173	.	.	.	0.28	5.4	19.2	1.0	20.0	19.2	1.2	25.1	19.2	1.2	23.5	19.2
Pb	118	65.9	.	.	.	0.0	0.0	55.6	1.1	31.	55.6	0.8	25.0	55.6	2.9	83.9	55.6
As	115	81.1	.	.	.	0.0	0.0	44.0	0.0	0.	44.0	0.0	0.0	44.0	0.5	16.2	44.0
Sn	58.3	44.7	.	.	.	0.82	46.8	39.1	0.8	45.7	39.1	0.8	46.8	39.1	0.7	44.6	39.1
Sb	55.5	53.7	.	.	.	0.22	13.3	23.2	0.1	11.	23.2	0.1	10.6	23.2	0.4	24.0	23.2
Na2SO4	.	.	.	.	.	1349			1207			1420			1349		

Table 51: Elemental and Sulphide sulphur calculations



Elemental & Sulphide sulphur calculations		
Original mass	3000	g
Mass after leach	2380	g
Mass reduction	620	g
	20.7	%
Total sulphides before	726.0	g S from Cu
	25.7	g S from Ni
	1.7	g S from Fe
	0.9	g S from Co
	754.4	g Sulphides Sulphur
But Total Sulphur	1113	g Sulphur
Thus, Total Elemental Sulphur	358.6	g S^0
% Elemental Sulphur	32.2	% S^o
Total sulphides after	579.5	g S from Cu
	25.5	g S from Ni
	2.5	g S from Fe
	0.8	g S from Co
	608.3	g Sulphides Sulphur
But Total Sulphur	603.8	g Sulphur
Thus, Total Elemental Sulphur	-4.5	g S^0

Appendix III

Table 52: Samples required for sulphuric acid pressure leach

	Element	Unit	Predicted value	Frequency	Sample size required(ml/ g)	Total samples	Total sample volume
Solution samples							
	Cu	g/L	0-40g/l	20/40/60/90/120/150/180/210/240	300	10	3000
	Ni	g/l	0-1000ppm	20/40/60/90/120/150/180/210/240	300	10	3000
	Fe^{2+}	g/L	0-3g/l	60/120/180/240	25	6	150
	Fe	g/L	0-3g/l	20/40/60/90/120/150/180/210/240	25	10	250
	H_2SO_4	g/L	60 - 180g/l	20/40/60/90/120/150/180/210/240	300	10	3000
	Pt	mg/L	<1ppm	60/120/150/180/210/240	300	10	3000
	Pd	mg/L	<1ppm	60/120/150/180/210/240	300	10	3000
	Rh	mg/L	<1ppm	60/120/150/180/210/240	300	10	3000
	Ru	mg/L	<1ppm	60/120/150/180/210/240	300	10	3000
Total	Se(iv)	mg/L	0-100ppm	60/120/150/180/210/240	300	10	3000
	Se(vi)	mg/L	????			0	0
	Te	mg/L	8-30ppm	60/120/150/180/210/240	300	10	3000
Product Solids(Filter Cake)							
	Ni	wt%	1-7%	Final solids only	20	1	20
	Co	wt%	0-0.5%	Final solids only	20	1	20
	Cu	wt%	5-25%	Final solids only	20	1	20
	Fe	wt%	???	Final solids only	20	1	20
	S Tot.	wt%	???	Final solids only	20	1	20
	Pb	wt%	0-1%	Final solids only	20	1	20
	As	wt%	0.34%	Final solids only	20	1	20
	Pt	g/t	0-1%	Final solids only	20	1	20
	Pd	g/t	0-5%	Final solids only	20	1	20
	Rh	g/t	0-1%	Final solids only	20	1	20
	Au	g/t	1%	Final solids only	20	1	20
	Ru	g/t	0-1%	Final solids only	20	1	20
	Se	g/t	0-25%	Final solids only	20	1	20
	Te	g/t	0-25%	Final solids only	20	1	20

Determine the sulphite concentration in solution

This is a rapid method of determining the sulphite concentration in solution. A blank must be done with every sample to standardise the Iodine standard solution. This is a back titration method checking the amount of iodine not converted.

Method

1 Pipette 1 ml sample into a suitable container

2 Pipette 50ml 0.1N colour Iodine and swirl to mix well

3 Add 100ml 20% HCL and mix well

4 Titrate with 0.1N Sodium Thiosulphate to a light yellow

5 Add a few millilitres 2g/l starch solution and titrate slowly, while mixing well, until the purple colour just disappear

6 Note reading on burette

7 Calculation

(Blank- titre) x 0.0040x1000

Aliquot taken (ml)

= g/l Total SO_3^{2-}

Determine the ferrous concentration in solution

This is a rapid method of determining the ferrous concentration in solution. This is a method where the ferrous in solution is titrated with potassium permanganate.

Method

1 Pipette sample into a suitable container

2 Acidify solution by adding 30 cm^3 of dilute sulphuric acid and 10cm3 phosphoric acid.

3 Dilute solution to $100cm^3$.

4 Titrate with potassium permanganate until the first permanent pink colour.

Sampling procedure

The following sampling procedure from the autoclave will apply:

(a) Open oxygen inlet valve on sample pot, then open discharge valve of autoclave and flush back sample line inside autoclave, then close both valves.

(b) Open vent valve on sample pot very slightly

(c) Open discharge valve of autoclave until solution comes out of sample pot vent valve, then close vent valve.

(d) Close discharge valve on autoclave.

(e) Cool down slightly and open the vent valve fully.

(f) Open drain valve on sample pot.

(g) Measure redox of slurry using a Ag/ AgCl probe.

(h) Measure volume and weight of sample for pulp density determination.

(i) Wash sample pot thoroughly with hot boiled water through vent valve.

(j) Close all valves on sample pot.

(k) Filter the slurry through a 0.45 micron filter paper under vacuum filtration.

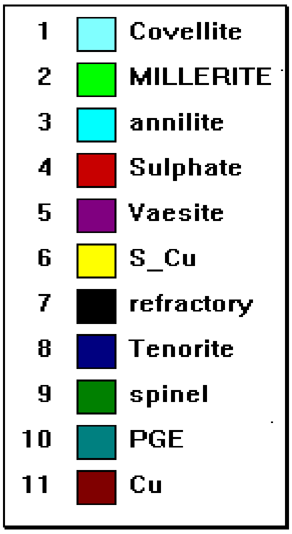
(l) Wash solids with demin water.

(m) Dry filter paper with solids at 60ºC and reweigh.

(n) Submit solution sample to laboratory and only final solids samples for assay.

Appendix IV

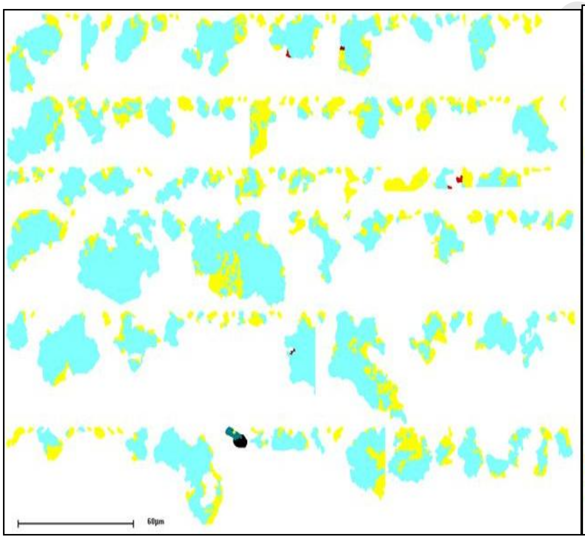
Mineralogy data

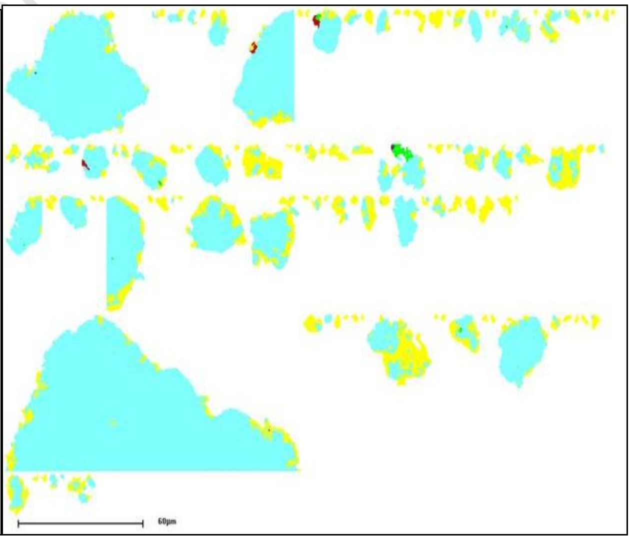


1	🟦	Covellite
2	🟩	MILLERITE
3	🟦	annilite
4	🟥	Sulphate
5	🟪	Vaesite
6	🟨	S_Cu
7	⬛	refractory
8	🟦	Tenorite
9	🟩	spinel
10	🟦	PGE
11	🟥	Cu

Figure 9: Key to interpreting the MLA maps

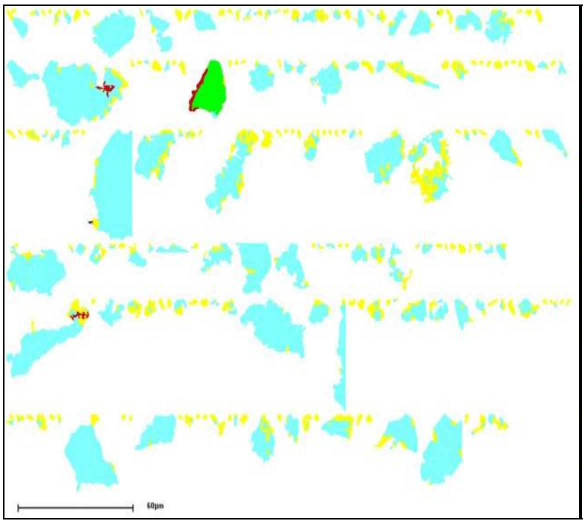
The scales on all of the MLA maps are 60 micon, only picture 19 was done at a 100 micron.



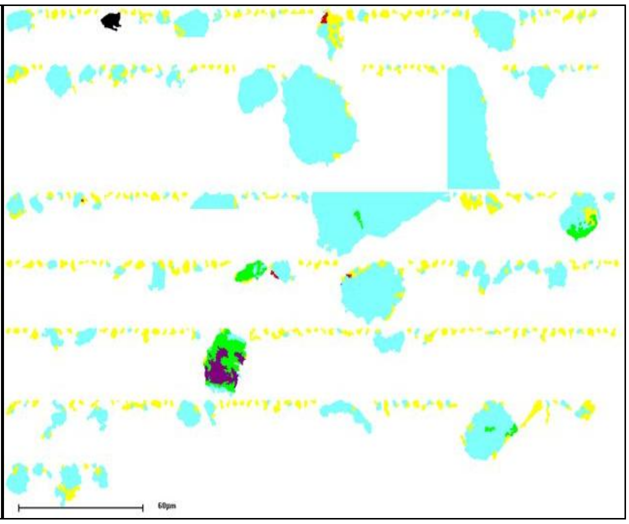


Picture 11: Residue B before H_2SO_4 leach

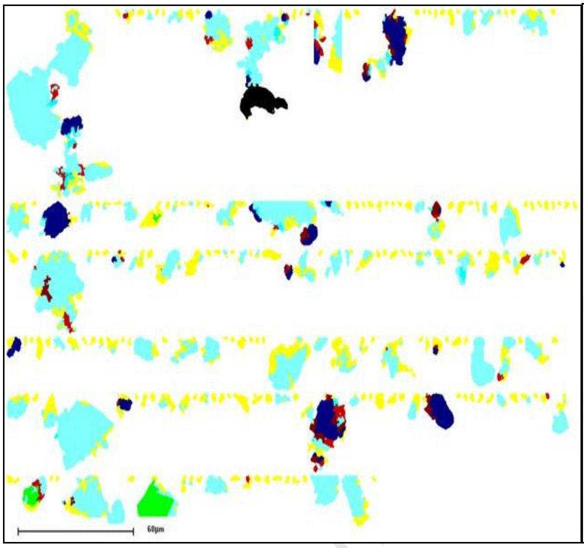
Picture 12: Residue B after H_2SO_4 leach



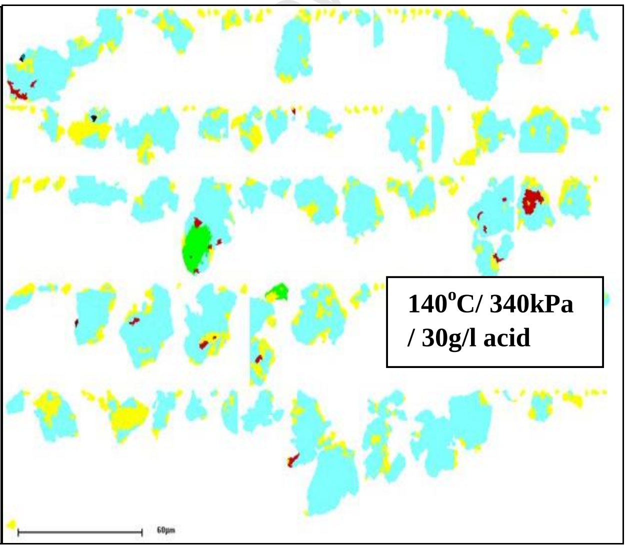
Picture 13: Residue A before H_2SO_4 leach



Picture 14: Residue A after H_2SO_4 leach

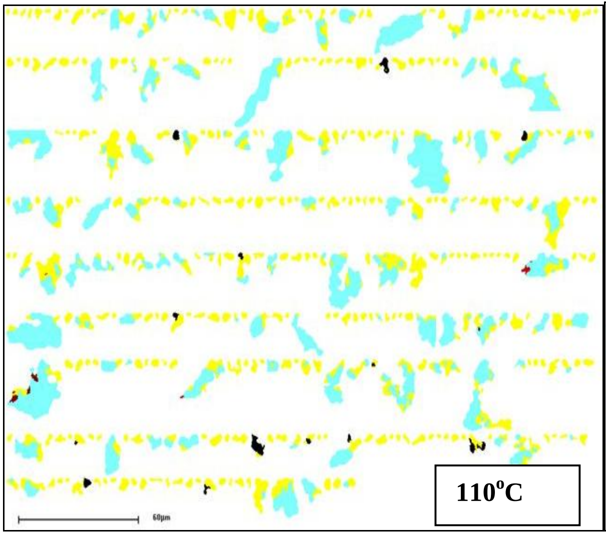


Picture 15: NaOH residue before H_2SO_4

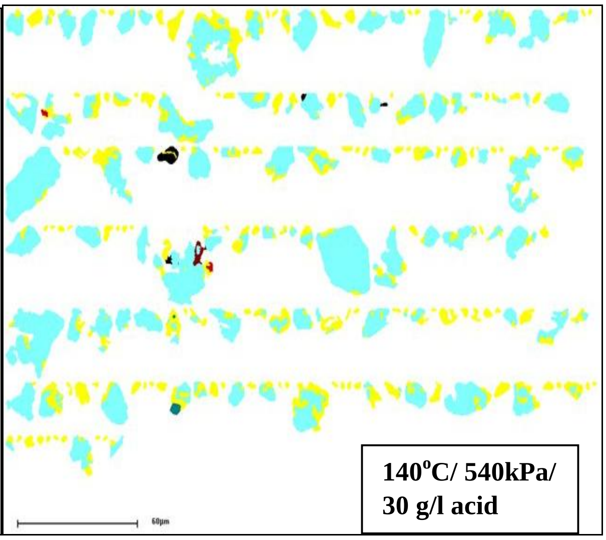


140°C/ 340kPa / 30g/l acid

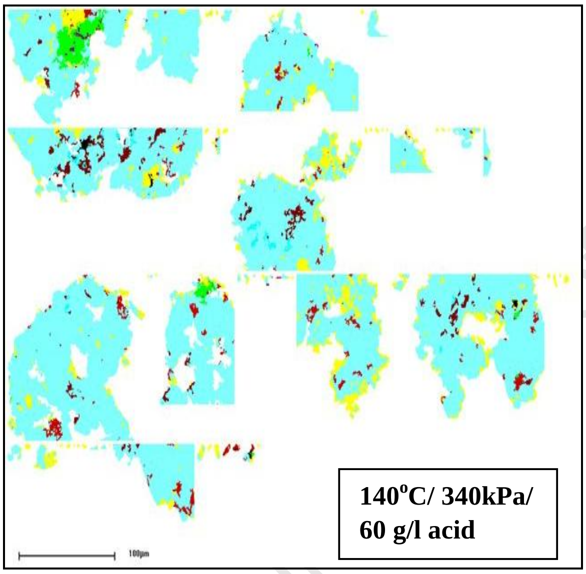
Picture 16: NaOH residue after H_2SO_4



Picture 17: NaOH residue after H_2SO_4



Picture 18: NaOH residue after H_2SO_4



Picture 19: NaOH residue after H_2SO_4

Appendix V

All results from sulphuric acid leach

Table 53: Sulphuric acid leach – Results from temperature variation

Temperature																
Time	% Ni extraction				% Cu extraction				% Fe precipitacion				Acid			
	110	130	140	150	110	130	140	150	110	130	140	150	110	130	140	150
0									0.0	0.9	0.9	0.9				
5		49.0	70.2	56.3		36.5	52.6	51.9		11.6	0.0	21.6		27.0		29.6
6	47.1				37.3				4.0				14.0			
11			70.1				53.4				0.0					
13		50.4		60.1		43.9		55.6		0.0		15.0		43.0		30.8
16	46.7				42.3				4.7				25.0			
19		50.6				48.0				0.0				44.0		
20			70.5	64.0			56.5	57.6			0.0	16.0			36.0	26.4
22	46.9				47.6				3.6				31.0			
25			77.7				61.8				0.0				33.0	
28		54.3				57.2				0.0				32.0		
30	56.6			64.8	58.5			59.1	0.0			15.3	30.0			27.9
35			77.1				61.2				0.0				30.0	
40		57.5				62.9				0.0				31.0		
56	63.8				68.5				0.0				30.0			
57			77.1				60.9				3.0				32.0	
60				61.4				59.3				19.6				28.8
68		57.8				64.9				0.0				32.0		
71	67.4				72.3				0.0				26.0			
85			80.2				64.4				0.6				33.0	
90				66.8				62.6				18.4				29.6
93	72.9				74.8				4.4				28.0			
98		56.9				66.8				1.9				33.0		
115			77.6				67.2				0.3				31.0	
120				68.6				64.9				19.3				28.6
123	78.4				80.9				9.7				27.0			
126		67.4				72.3				0.0				32.0		
145			80.7				65.5				3.7				34.0	
149		69.5				74.8				0.0				31.0		
150				80.1				68.0				17.7				29.4
151	83.4				80.6				7.1				27.0			
175			83.4				65.9				0.0				31.0	
179	87.2	70.5			85.0	74.7			6.8	1.5			28.0	29.0		
180				76.6				68.1				18.0				28.9
205			85.0				70.3				0.0				32.0	
207		75.9				80.7				0.0				31.0		
210				81.0				71.8				16.4				29.4
211	88.7				87.7				6.5				27.0			
237		80.8				85.3				0.0				32.0		
240			85.5	86.5			70.5	72.3			0.0	18.5			30.0	30.6
255	93.7				90.9				5.2				28.0			
267		84.1				86.8				0.0				27.0		
295		86.8				88.7				0.0				32.0		
302	90.8				91.6				9.6				26.0			
Final	91.8	86.9	87.0	86.8	92.3	88.1	72.3	72.2								

Table 54: Sulphuric acid leach – Results from temperature variation

	Temperature											
Time	**Redox**				**Ferrous concentration**				**Total Fe/ Ferrous ratio**			
	110	**130**	**140**	**150**	**110**	**130**	**140**	**150**	**110**	**130**	**140**	**150**
0					2000.0	2000.0	2000.0	2000.0	0.000	0.000	0.000	0.000
5		424	437.0	429		1034.5	1266.7	929.9		0.724	0.674	0.700
6	428.0				991.9				0.822			
11			449.0				1161.1				0.821	
13		426		446		1308.9		888.6		0.574		0.944
16	407.0				1405.2				0.287			
19		420				1266.7				0.683		
20			464.0	458			992.2	764.6			1.080	1.250
22	402.0				1405.2				0.313			
25			469.0				950.0				1.361	
28		422				1308.9				0.728		
30	405.0			459	1611.8			640.6	0.278			1.725
35			474.0				865.6				1.471	
40		424				1224.5				0.889		
56	410.0				1446.5				0.445			
57			480.0				612.2				2.316	
60				479				454.6				2.672
68		440				897.2				1.450		
71	412.0				1239.9				0.595			
85			485.0				527.8				2.970	
90				483				372.0				3.592
93	417.0				1177.9				0.606			
98		449				717.8				1.880		
115			479.0				591.1				2.581	
120				485				330.6				4.149
123	417.0				929.9				0.938			
126		441				865.6				1.464		
145			484.0				485.6				3.244	
149		437				844.5				1.549		
150				487				382.3				3.573
151	421.0				867.9				1.154			
175			500.0				422.2				4.210	
179	440.0	437			826.6	707.2			1.289	2.004		
180				496				310.0				4.647
205			505.0				358.9				5.065	
207		457				717.8				2.034		
210				503				248.0				6.268
211	440.0				805.9				1.375			
237		463				686.1				2.264		
240			503.0	507			337.8	206.6			5.611	7.568
255	451.0				702.6				1.786			
267		456				633.3				2.556		
295		467				591.1				2.818		
302	454.0				619.9				2.051			
Final												

Final results			
	110	**130**	**140**
Cu	93.0	88.7	72.7
Ni	92.4	87.2	87.1
Co			
Fe			
%S_{Tot}	33.3	32.0	33.1
%S^0	85.4	77.9	48.9
%S^{2-}	14.6	22.1	51.1
Pt			
Pd			
Rh			4.8
Au			
Ru	15.9	19.4	30.5
Ir			
Pb	15.6	22.2	32.0
Sb	12.8	11.7	17.5
As	-46.4	-46.5	-48.7
Bi	-46.7	-42.6	-42.7
Sn	-62.5	-65.6	-63.3
Mn			
Se	50.3	27.0	22.7
Te	59.9	58.4	51.5
Mass Loss	76	73	63.97142857
Redox	454	467	503

Pt	<0.1	<0.1	<0.1
Pd	<0.1	<0.1	<0.1
Rh	<0.1	<0.1	0.10
Au	0.00	0.00	0.00
Ru	0.50	0.50	0.70
Ir	<0.1	<0.1	<0.1

Table 55: Sulphuric acid leach – Results from agitation variation

Agitation																
Time	**% Ni extraction**				**% Cu extraction**				**% Fe precipitation**				**Acid**			
	30	**40**	**50**	**60**	**30**	**40**	**50**	**60**	**30**	**40**	**50**	**60**	**30**	**40**	**50**	**60**
0									0.9	0.9	0.9	0.9				
3			50.3				35.9				13.9				21	
5	50.4	70.2		51.4	39.6	52.6		46.1	-0.1	-5.1		-4.1	19			16
11		70.1				53.4				-4.0						
12	51.0				42.8				-2.4				31			
13			59.1				44.4				0.4				26	
15				51.3				48.9				-4.6				28
18	52.1				45.8				-3.1				33			
20		70.5	61.8			56.5	46.2			-0.8	-2.9			36	29	
25		77.7				61.8				-8.8				33		
29				54.9				51.8				-9.0				29
35		77.1	63.4			61.2	48.3			-3.0	-0.3			30	30	
38	61.6				52.3				-2.2				33			
53				59.6				55.9				-10.9				28
57		77.1				60.9				3.0				32		
65			69.3				56.9				-2.7				30	
68	69.0				60.4				-3.7				34			
83				63.8				60.7				-2.7				29
85		80.2				64.4				0.6				33		
95			71.6				59.3				-2.3				31	
98	75.1				67.3				-7.7				33			
113				64.9				62.3				-2.0				29
115		77.6				67.2				0.3				31		
125			72.9				63.3				-2.6				31	
128	75.1				68.4				-6.7				33			
143				69.2				65.4				-6.5				29
145		80.7				65.5				3.7				34		
155			74.7				65.5				-2.2				31	
158	78.8				72.6				-9.9				33			
173				68.8				64.9				-10.3				31
175		83.4				65.9				-2.0				31		
185			78.6				70.5				-5.7				32	
188	76.4				72.0				-5.3				33			
203				71.0				68.2				-8.3				29
205		85.0				70.3				-0.2				32		
215			79.4				70.6				-4.9				31	
218	81.5				78.1				-11.8				33			
233				72.1				72.2				-7.7				29
240		85.5				70.5				-2.8				30		
245			78.6				73.1				-5.3				31	
248	82.2				79.1				-10.6				32			
263				74.9				74.3				-12.6				28
293								76.4				-18.2				29
300	84.9			77.1	81.0				-13.3				32			
Final	85.0	87.0	78.1	77.4	80.7	72.3	73.1	76.1								

Table 56: Sulphuric acid leach – Results from agitation variation

Time	**Agitation**																								
	Redox				**Ferrous concentration**				**Total Fe/ Ferrous ratio**									**% Se extraction**				**% Te extraction**			
	30	**40**	**50**	**60**	**30**	**40**	**50**	**60**	**30**	**40**	**50**	**60**		**30**	**40**	**50**	**60**	**30**	**40**	**50**	**60**	**30**	**40**	**50**	**60**
0					2000	2000.0	2000.0	2000.0	0.000	0.000	0.000	0.000													0.000
3			437				1198.5				0.450		**Cu**	81.0	72.7	73.1	76.6			0.9				6.3	
5	431	437.0		438	1106	1266.7		1105.6	0.827	0.674		0.900	**Ni**	85.0	87.1	78.7	77.7	0.8				5.7			11.561
11		449.0				1161.1				0.821			**Co**												
12	438				1064				0.917				**Fe**					0.3				8.8			
13			444				1053.9				0.907		**$\%S_{Tot}$**	40.5	33.1	28.6	39.8			0.5				9.2	
15				447				1002.2				1.105	**$\%S^{0}$**	59.6	48.9	53.1	50.4								17.671
18	432				1095				0.852				**$\%S^{2-}$**	40.4	51.1	46.9	49.6	0.3				9.7			
20		464.0	452			992.2	929.9			1.080	1.233		**Pt**							0.5				10.1	
25		469.0				950.0				1.361			**Pd**												
29				455				950.6				1.313	**Rh**		4.8	4.3	10.1								23.947
35		474.0	460			865.6	681.9			1.471	1.967		**Au**							0.5				10.5	
38	442				909				1.183				**Ru**	26.1	30.5	23.9	32.3	0.4				10.9			
53				467				723.3				2.094	**Ir**												24.608
57		480.0				612.2				2.316			**Pb**	21.3	32.0	13.0	26.4								
65			463				743.9				1.787		**Sb**	13.1	17.5	12.0	13.9			0.5				12.8	
68	445				744				1.676				**As**	-54.9	-48.7	-67.4	-56.8	0.4				13.1			
83				474				619.9				2.342	**Bi**	-38.7	-42.7	-44.2	-39.2								25.268
85		485.0				527.8				2.970			**Sn**	-57.6	-63.3	-65.5	-52.1								
95			474				619.9				2.328		**Mn**							0.6				13.2	
98	462				620				2.293				**Se**	29.3	22.7	21.2	30.4	0.6				14.8			
113				484				516.6				2.984	**Te**	58.5	51.5	52.1	58.4								25.929
115		479.0				591.1				2.581			**Mass Loss**	71.2	64.0	64.0	69.4								
125			480				537.3				2.854		**Redox**	499.0	503.0	487.0	492.0			0.6				15.2	
128	469				558				2.581									0.6				15.4			
143				494				454.6				3.729													26.590
145		484.0				485.6				3.244			**Pt**	<1	<0.1	<1	<1								
155			485				475.3				3.340		**Pd**	<1	<0.1	<1	<1			0.6				16.1	
158	478				455				3.471				**Rh**	<1	0.1	0.1	0.2	0.6				16.6			
173				491				434.0				4.131	**Au**												26.590
175		500.0				422.2				4.210			**Ru**	0.6	0.7	0.6	0.7								
185			493				372.0				4.732		**Ir**	<1	<0.1	<1	<1			0.7				17.3	
188	476				455				3.236									0.7				16.8			
203				491				434.0				4.037													33.856
205		505.0				358.9				5.065															
215			499				330.6				5.403									0.7				17.6	
218	480				434				3.665									0.8				18.6			
233				484				516.6				3.206													34.682
240		503.0				337.8				5.611															
245			487				372.0				4.710									0.7				18.4	
248	485				372				4.331									0.7				18.6			
263				496				392.6				4.789													35.508
293				492				392.6				5.072													36.334
300	499				269				6.443									0.8				19.9			
Final																									

Table 57: Sulphuric acid leach – Results from acid concentration variation

Acid conc.																
Time	**% Ni extraction**				**% Cu extraction**				**% Fe precipitation**				**Acid**			
	20	**40**	**60**	**80**	**20**	**40**	**60**	**80**	**20**	**40**	**60**	**80**	**20**	**40**	**60**	**80**
0									0.0	0.9	0.9	0.0	0	0.0	0.0	0
2				60.9				41.9				4.9				24
5		70.2				52.6				-5.1						
6	47.7				41.0				31.4				7			
11		70.1				53.4				-4.0						
17	48.5			60.0	44.7			47.8	17.4			-0.4	12			49
20		70.5	52.3			56.5	48.5			-0.8	-1.0			36.0		
25		77.7				61.8				-8.8				33.0		
29				60.1				49.0				5.1				62
30	59.3				49.8				9.8				14			
35		77.1				61.2				-3.0				30.0		
40			56.3				51.1				1.5				53.0	
57		77.1				60.9				3.0				32.0		
59				65.9				56.8				2.5				60
60	68.8		64.6		54.5		56.9		10.1		1.1		14		52.0	
84			69.0				60.9				2.8				56.0	
85		80.2				64.4				0.6				33.0		
89				69.3				59.7				3.2				59
90	75.9				57.1				6.3				14			
104			70.4				63.4				2.1				52.0	
115		77.6				67.2				0.3				31.0		
119				68.9				62.9				6.1				59
120	78.4				59.5				14.6				14			
121			72.3				63.8				2.2				52.0	
145		80.7				65.5				3.7				34.0		
149				72.8				64.8				2.8				59
150	79.9		76.7		60.8		67.9		10.5		3.4		15		51.0	
175		83.4				65.9				-2.0				31.0		
179				73.0				67.4				4.5				63
180	80.3		80.2		62.5		72.5		10.4		3.5		15		53.0	
205		85.0				70.3				-0.2				32.0		
209				74.2				69.4				3.2				60
210	82.2		81.3		64.9		74.1		9.2		-4.7		15		53.0	
239				74.3				71.7				3.9				61
240	83.6	85.5	80.8		68.3	70.5	74.8		8.0	-2.8	-4.4		15	30.0	53.0	
269	84.5			79.7	68.8			76.5	6.8			-1.7	16			60
299	86.4			80.4	73.5			76.9	6.4			-1.9	15			61
Final	86.3	87.0	81.0	80.3	73.3	72.3	75.7	76.3								

Table 58: Sulphuric acid leach – Results from acid concentration variation

Time	Acid conc.																								
	Redox				Ferrous concentration				Total Fe/ Ferrous ratio									% Se extraction				% Te extraction			
	20	40	60	80	20	40	60	80	20	40	60	80		15	30	50	60	2	4	6	8	2	4	6	8
0					2000	2000	2000	2000	0.0	0.0	0.0	0.0													
2				434				1095				0.8	C	73.5	72.7	75.5	76.9				0.44				2.4
5		437				1267				0.7			N	86.5	87.1	81.1	80.4								
6	418				971				0.4				C					0.109				1.189			
11		449				1161				0.8			F												
17	447			447	847			868	1.0			1.3	%S$_{T}$	38.5	33.1	18.0	27.6	0.438			0.12	2.412			3.7
20		464	441			992	961			1.1	1.1		%S	46.3	48.9	63.0	59.2								
25		469				950				1.4			%S^{2}	53.7	51.1	37.0	40.8								
29				463				754				1.5	P								0.13				3.8
30	450				785				1.3				P					0.450				2.480			
35		474				866				1.5			R	8.3	4.8	4.0									
40			453				760				1.6		A												
57		480				612				2.3			R	26.8	30.5	25.7	23.3								
59				465				661				2.0	I								0.13				5.1
60	459		467		620		654		1.9		2.1		P	21.9	32.0	35.9	19.0	0.468				3.737			
84			476				718				1.8		S	3.8	17.5	22.0	23.3								
85		485				528				3.0			A	-63.2	-48.7	-67.4	-62.0								
89				478				517				2.8	B	-39.1	-42.7	-51.1	-42.7				0.13				5.2
90	474				475				3.0				S	-61.9	-63.3	-55.6	-46.3	0.475				3.839			
104			488				570				2.6		M												
115		479				591				2.6			S	21.2	22.7	10.0	21.1								
119				480				475				3.0	T	59.0	51.5	44.3	52.				0.1				5.
120	477				475				2.6				Mass Los	64.3	64.0	63.0	66.	0.48				3.94			
121			501				464				3.4		Redo	494	503	517	513								
145		484				486				3.2															
149				491				372				4.3									0.1				5.
150	484		489		393		591		3.6		2.4		P	<1	<0.1	<1	<1								
175		500				422				4.2			P	<1	<0.1	<1	<1								
179				490				341				4.7	R	0.2	0.1	0.1	<1				0.14				5.6
180	483		491		393		591		3.6		2.5		A					0.500				4.043			
205		505				359				5.1			R	0.7	0.7	0.7	0.6								
209				500				310				5.3	I	<1	<0.1	<1	<1				0.14				5.8
210	485		497		372		528		3.9		3.2							0.513				4.145			
239				475				413				3.7									0.15				7.1
240	497	503	517		331	338	359		4.6	5.6	5.3							0.525				4.247			
269	500			505	310			289	5.1			6.1						0.537			0.15	5.538			7.3
299	494			513	372			248	4.1			7.3						0.55				5.67			
Final																									

Table 59: Sulphuric acid leach – Results from oxygen partial pressure variation

Oxygen																
Time	**% Ni extraction**				**% Cu extraction**				**% Fe precipitation**				**Acid**			
	140	**340**	**540**		**140**	**340**	**540**		**140**	**340**	**540**		**140**	**340**	**540**	
Start									**0**	**0**	**0**	**0**			0	
At temp			84.4				35.6				93.0				0	
O_2 open			94.6				44.2				95.6				0	
Acid add															0	
5		70.2				52.6				-5.1						
6	54.6				45.2				-3.1				21.9			
10			88.1				64.9				47.9				18	
11		70.1				53.4				-4.0						
15	54.8				48.2				-3.1				27.9			
20		70.5				56.5				-0.8				36.0		
23			88.2				69.0				9.1				35	
24	53.8				49.4				-1.9				31.0			
25		77.7				61.8				-8.8				33.0		
34	55.7				51.7				-1.5				33.0			
35		77.1				61.2				-3.0				30.0		
57		77.1				60.9				3.0				32.0		
60			87.3				69.3				5.2				40	
65	61.1				61.1				-3.4				35.0			
85		80.2				64.4				0.6				33.0		
90			88.9				71.7				5.7				41	
95	66.0				62.5				-4.8				37.0			
115		77.6				67.2				0.3				31.0		
120			88.9				71.2				12.1				41	
125	70.4				68.0				-8.1				36.0			
145		80.7				65.5				3.7				34.0		
150			87.3				71.0				11.2				41	
155	71.5				72.7				-7.0				35.0			
175		83.4				65.9				-2.0				31.0		
180			89.2				70.0				11.3				41	
185	71.9				72.8				-4.2				35.0			
205		85.0				70.3				-0.2				32.0		
210			92.2				74.1				8.3				43	
215	74.0				76.3				-6.4				35.0			
240		85.5	90.6			70.5	70.2			-2.8	7.2			30.0	41	
245	74.4				78.6				-6.4				35.0			
270			93.9				73.2				5.5				41	
275	75.9				79.9				-7.4				35.0			
300			97.8				81.1				17.6				38	
305	74.4				78.3				-5.1				35.0			
Final		87.0	97.2			72.3	80.9									

Table 60: Sulphuric acid leach – Results from oxygen partial pressure variation

	Oxygen																								
Time	Redox				Ferrous concentration				Total Fe/ Ferrous ratio									% Se extraction				% Te extraction			
	140	340	540		140	340	540		140	340	540			140	340	540		14	34	54		14	34	54	
Start					2000	2000	2000		0.00	0.00	0.00											1.0	1.0	1.0	
At temp			367.0				165.3				-0.1		Cu	78.1	72.7	81.2									
O_2 open			362.0				144.7				-0.4		Ni	74.4	87.1	97.2									
Acid add													Co												
5		437.0				1266.7				0.7			Fe												
6	436.0				1198.5				0.7				$\%S_{To}$	39.3	33.1	65.6		0.43				4.8			
10			467.0				423.6				1.5		%S	54.8	48.9	31.9									
11		449.0				1161.1				0.8			$\%S^{2}$	45.2	51.1	68.1									
15	446.0				1115.9				0.9				P			2.4		0.23				4.9			
20		464.0				992.2				1.1			Pd			0.1									
23			494.0				434.0				3.4		Rh		4.8	9.3									
24	451.0				950.6				1.2				Au		0.0	0.0		0.24				5.0			
25		469.0				950.0				1.4			Ru		30.5	25.5									
34	465.0				847.2				1.4				Ir			6.9		0.24				5.2			
35		474.0				865.6				1.5			Pb		32.0	20.8									
57		480.0				612.2				2.3			Sb		17.5	12.8									
60			509.0				310.0				5.5		As												
65	457.0				867.9				1.4				B					0.47				5.3			
85		485.0				527.8				3.0			Sn												
90			527.0				289.3				6.0		Mn												
95	479.0				619.9				2.4				Se	27.5	22.7	36.0		0.48				6.6			
115		479.0				591.1				2.6			Te	56.3	51.5	71.9									
120			534.0				248.0				6.7		Mass Loss	68.4	64.0	77.									
125	475.0				578.6				2.8				Redox	487	503	524		0.49				8.0			
145		484.0				485.6				3.2															
150			538.0				268.6				6.3														
155	473.0				661.3				2.3				P		<0.1	0.05		0.29				8.2			
175		500.0				422.2				4.2			Pd		<0.1	0.05									
180			533.0				248.0				6.9		Rh		0.10	0.20									
185	469.0				475.3				3.4				Au					0.51				8.4			
205		505.0				358.9				5.1			Ru		0.70	0.60							27.2		
210			538.0				268.6				6.7		Ir		<0.1	0.05									
215	490.0				454.6				3.7									0.52				8.6			
240		503.0	520.0			337.8	248.0			5.6	7.5												27.7		
245	487.0				413.3				4.2									0.53				8.8			
270			524.0				248.0				7.8														
275	498.0				351.3				5.2									0.55				9.0			
300			524.0				310.0				5.3														
305	487.0				310.0				5.8									0.5				9.			
Final																									

Table 61: Sulphuric acid leach – Results from Ferrous concentration variation

Ferrous																
Time	% Ni extraction				% Cu extraction				% Fe precipitation				Acid			
	0	1	2	3	0	1	2	3	0	1	2	3	0	1	2	3
Start	0			0	0			0	0	**0**	**0**	0	0			0
At temp	75.0			45.6	6.3			18.8	44.5			45.6	0			0
O_2 open	77.1			61.9	13.0			35.7	70.6			83.3	0			0
Acid add													0			0
4				75.7				66.3				29.1				43
5			70.2				52.6				0.0					
6	90.4				46.6				64.3				38			
11			70.1				53.4				0.0					
13	91.2				48.8				69.0				46			
16				74.4				68.4				5.5				58
20		52.2	70.5			44.9	56.5			11.1	0.0				36	
25			77.7				61.8				0.0				33	
30	91.0				54.3				62.7				32			
32				74.0				69.3				0.0				43
35			77.1				61.2				0.0				30	
40		57.0				47.2				15.3				35		
45	94.2				61.6				39.7				37			
57			77.1				60.9				3.0				32	
60		65.2				47.8				18.0				33		
62				75.0				69.1				-1.2				39
75	92.4				66.3				27.2				38			
80		66.1				53.9				14.0				34		
85			80.2				64.4				0.6				33	
92				78.4				74.4				0.0				39
100		74.8				54.0				19.1				34		
105	94.1				69.9				0.0				34			
115			77.6				67.2				0.3				31	
120		71.5				57.5				17.6				33		
122				78.5				74.6				0.0				38
135	96.1				73.8				0.0				35			
140		78.3				62.5				12.7				33		
145			80.7				65.5				3.7				34	
152				78.1				73.8				0.0				39
160		75.7				60.2				16.4				33		
165	96.9				75.3				0.0				35			
175			83.4				65.9				0.0				31	
180		80.3				62.7				15.7				34		
182				78.7				73.4				0.0				39
195	98.9				78.2				0.0				35			
205			85.0				70.3				0.0				32	
210		79.3				63.4				16.2				35		
212				80.1				77.7				0.0				39
225	100.0				79.9				0.0				35			
240		87.4	85.5			69.2	70.5			11.2	0.0			36	30	
242				88.7				76.6				0.0				38
255	100.0				81.7				0.0				35			
285	100.0				83.9				0.0				35			
Final	100.0	87.4	87.0	88.4	83.3	68.9	72.3	76.3								

Table 62: Sulphuric acid leach – Results from Ferrous concentration variation

	Ferrous																								
Time	Redox				Ferrous concentration				Total Fe/ Ferrous ratio									% Se extraction				% Te extraction			
	0	1	2	3	0	1	2	3		1	2														
Start					0	100	200	300																	
At temp	213.0			273.	82.			1487.	0.			0.	C	83.	69.	72.	76.	1.2			0.2	0.0			0.0
O $_2$ open	327.0			352.0	41.3			475.3	0.0			0.1	Ni	97.6	87.0	87.1	88.6	1.03			0.26	1.19			1.37
Acid add													C												
4				475.				909.				1.	F								1.3				4.1
5			437.0				1266.7				0.7		%S$_{T}$	74.8	42.8	33.1	56.6			0.00				0.00	
6	414.0				62.0				0.0				%S	22.	33.	48.	32.	3.4				8.6			
11			449.0				1161.1				0.8		%S^{2}	77.	67.	51.	67.			0.0				0.0	
13	392.0				82.				0.				P	2.	2.		2.	1.4				8.8			
16				489.0				929.9				2.1	P	0.1	0.1		0.1				1.08				7.05
20		433.0	464.0			654.5	992.2			0.4	1.1		R	2.5	4.5	4.8	9.6		0.00	0.00			0.00	0.00	
25			469.				950.				1.		A	0.	0.	0.	0.			0.0				0.0	
30	403.0				82.				0.				R	13.	32.	30.	30.	1.5				9.0			
32				501.				929.				2.	I	7.	6.		7.				0.8				9.9
35			474.0				865.6				1.5		P	22.1	53.4	32.0	25.2			0.00				0.00	
40		414.0				485.				0.			S	22.	24.	17.	13.		0.0				0.0		
45	389.0				103.				0.				A					1.0				9.3			
57			480.0				612.2				2.3		B							0.00				0.00	
60		454.0				443.3				0.9			S						0.00				0.00		
62				521.				516.				5.	M								0.8				13.0
75	390.0				103.				0.				S	49.		22.	32.	1.0				9.5			
80		464.0				443.3				1.1			T	65.7		51.5	66.4		0.00				0.00		
85			485.0				527.8				3.0		Mass Los	81.5	70.3	64.0	72.9			0.00				0.00	
92				530.0				434.0				6.8	Redo	470	486	503	536				0.90				13.36
100		470.0				443.3				1.0									0.00				0.00		
105	426.0				103.				0.									1.3				10.9			
115			479.				591.1				2.		P	0.0	0.0	<0.	0.0			0.0				0.0	
120		481.0				422.2				1.1			P	0.0	0.0	<0.	0.0		0.0				0.0		
122				535.				413.				6.	R	0.0	0.1	0.1	0.2				0.9				13.7
135	432.0				82.				0.				A					1.3				11.2			
140		487.0				337.				1.			R	0.3	0.8	0.7	0.7		0.0				0.0		
145			484.				485.				3.		I	0.0	0.0	<0.	0.0			0.0				0.0	
152				537.				330.				8.									0.9				14.0
160		484.0				380.				1.5									0.0				0.0		
165	441.0				124.0				0.0									1.40				11.52			
175			500.0				422.2				4.2									0.00				0.00	
180		482.0				380.				1.5									0.0				0.0		
182				536.				310.				9.									0.9				14.4
195	447.0				124.0				0.0									1.43				11.79			
205			505.				358.				5.									1.0				27.2	
210		485.0				316.7				2.1									0.0				0.0		
212				537.				310.				10.									0.9				14.7
225	451.0				103.				0.									1.4				12.0			
240		486.0	503.0				337.8				5.6								0.00	1.01			0.00	27.66	
242				536.0				351.3				8.5									1.01				15.16
255	461.0				124.				0.									1.2				12.3			
285	470.0				103.				0.									1.3				12.6			
Final																									

Table 63: Sulphuric acid leach – Results from residue comparison

Comparison between Residues

Time	% Ni extraction			% Cu extraction			% Fe precipitation			Acid		
	NaOH	A	B	NaOH	A	B	NaOH	A	B	NaOH	A	B
Start							**0**	**0**	**0**			
At temp		11.0	11.8		1.5	0.4		12.2	5.1			
O_2 open		16.4	14.4		25.2	4.0		87.5	69.7			
Acid add												
5	70.2			52.6			0.0					
7			17.7			8.6			63.7			19
9		23.1			35.9			57.9			20	
11	70.1			53.4			0.0					
20	70.5			56.5			0.0			36		
24			18.2			12.2			8.4			44
25	77.7	33.7		61.8	44.6		0.0	14.8		33	33	
35	77.1			61.2			0.0			30		
43		35.6			46.2			3.3			41	
57	77.1		19.4	60.9		12.6	3.0		1.9	32		44
75		37.6			49.0			2.2			42	
84			19.2			13.2			0.0			44
85	80.2			64.4			0.6			33		
105		40.9			51.7			0.8			46	
114			20.4			13.1			0.3			44
115	77.6			67.2			0.3			31		
135		43.5			50.8			1.7			47	
144			22.1			13.3			0.0			44
145	80.7			65.5			3.7			34		
173		48.0			51.8			0.0			46	
175	83.4			65.9			0.0			31		
195		50.2			53.2			0.0			47	
205	85.0			70.3			0.0			32		
225		51.2			54.6			0.0			47	
240	85.5			70.5			0.0			30		
256		57.5			57.2			0.0			47	
Final	87.0	61.7	27.4	72.3	57.3	13.9						

Table 64: Sulphuric acid leach – Results from residue comparison

	Comparison between Residues																								
Time	Redox				Ferrous concentration				Total Fe/ Ferrous ratio									% Se extraction				% Te extraction			
	NaOH	A	B		NaO	A	E		NaO					NaO				NaO				NaO			
Start					200	200	200																		
At temp		281.0	254.0			1532.2	1631.1			0.2	0.3		Cu	72.7	57.6	11.1			0.1						
O₂ open		373.0	401.0			227.4	514.0			0.1	0.3		Ni	87.1	61.2	27.5			0.4				0.1		
Acid add													C												
5	437.0				1266.7				0.7				F												
7			471.0				355.9				1.3		%S$_{T}$	33.1	41.7	11.6									
9		449.0				435.0				1.0			%S	48.9	37.3	66.5			0.6				0.0		
11	449.0				1161.1				0.8				%S	51.1	62.7	33.5									
20	464.0				992.2				1.1				P		2.6	1.3									
24			510.0				336.1				5.1		P		0.1	0.1									
25	469.0	487.0			950.0	504.2			1.4	2.5			R	4.8	2.7	3.4			0.8				0.9		
35	474.0				865.6				1.5				A												
43		499.0				454.7				3.4			R	30.5	19.7	8.4			0.6				2.7		
57	480.0		525.0		612.2		266.9		2.3		7.3		I		7.8	3.8									
75		496.0				375.6				4.4			P	32.0	17.7	10.5			0.8				5.6		
84			528.				286.				7.		S	17.	12.	6.									
85	485.0				527.8				3.0				A												
105		515.0				276.8				6.5			B						0.7				7.1		
114			532.0				257.0				8.0		S												
115	479.0				591.1				2.6				M												
135		527.0				227.4				8.2			S	22.7	21.7	2.0			0.7				7.3		
144			539.				247.				8.		T	51.	46.	25.									
145	484.				485.				3.				Mass Los	64.	51.	9.									
173		536.0				197.7				10.1			Redo	503	539	539			0.7				8.8		
175	500.0				422.2				4.2																
195		537.0				197.7				10.2									0.6				9.1		
205	505.0				358.9				5.1									1.0				27.2			
225		545.0				168.1				12.3									0.7				9.3		
240	503.0				337.8				5.6									1.0				27.7			
256		539.0				177.9				11.7									0.6				9.5		
Final																									