



An experimental evaluation of the leaching kinetics of PGM-containing Ni–Cu–Fe–S Peirce Smith converter matte, under atmospheric leach conditions

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ABSTRACT

In a first stage atmospheric leach in a typical Sherritt Ni–Cu matte leach process, a Ni–Cu–Fe–S Peirce Smith converter matte is contacted with recycled copper spent electrolyte (an aqueous copper sulphate/sulphuric acid solution) at 85 °C with the purpose of dissolving nickel, while simultaneously removing copper from solution. In the PGM industry, copper removal is also important because it serves as a leading indicator in the removal of Ir, Rh, and Ru from the spent electrolyte. The matte mainly consists of heazlewoodite, chalcocite/djurleite, a Ni–Cu alloy phase and inert spinel minerals (magnetite and trevorite). Nickel is leached from the matte by two mechanisms: (i) leaching by sulphuric acid and oxygen; and (ii) an anaerobic metal exchange reaction (cementation and metathesis) between cupric ions in solution and nickel in the matte, which is also responsible for the removal of copper from solution.

This study investigates the oxidative and non-oxidative leaching of converter matte in a laboratory batch reactor, with attention specifically being given to the effects of initial copper and acid concentrations and their effects on leaching kinetics. Experimental conditions were varied based on a 2^N experimental design. The availability of oxygen for acid-leaching reactions was found to be the most important factor influencing copper removal and nickel extraction. A 63% nickel extraction could be achieved during oxidative tests vs. 22% in a non-oxidative test. This also indicates that cementation did not take place to a significant degree and that nickel leaching mostly took place via leaching by acid and oxygen. It is suspected that the low degree of copper removal can be attributed to the solids/reactants ratio was employed in tests. The initial copper and acid concentrations did not have a significant effect on the rate of nickel extraction or the total amount of nickel extracted. The rate of copper removal was not significantly influenced by the initial copper concentration, but copper removal was affected by the initial acid concentration. In oxidative tests with high initial acid concentrations, the rate at which copper was leached from the matte was faster than the rate of cementation. The results suggest that operating under high initial acid conditions could interfere with copper removal with no significant benefit in terms of nickel extraction. The results allow the regression of rate expressions.

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1. Introduction

In the recovery of platinum-group metals (PGMs) from the Bushveld Igneous Complex in South Africa, base metals are often recovered as by-products. This is also the case at the Lonmin Marikana refinery, located near Rustenburg, where ores from both the Merensky and UG2 reefs are processed to produce PGM's. Nickel and copper are the most important by-products.

Flotation concentrate from the mine undergoes smelting, followed by Pierce Smith converting, with the purpose of lowering iron and sulphur concentrations. A high purity Ni–Cu–S matte is

produced which also contains the bulk of the PGMs. Typically, the most significant phases in converter matte are heazlewoodite (Ni₃S₂), chalcocite (Cu₂S), a Cu–Ni alloy, and entrained inert minerals such as trevorite and magnetite and entrained fayalitic slag. A detailed discussion of the mineralogy and microstructure is presented by Thyse et al. (in press). The matte is granulated and milled in a closed ball milling circuit, after which the milled matte is subjected to a series of selective leaching steps. Recovery processes such as electrowinning and crystallization are used to recover the Cu as cathode and the NiSO₄·6H₂O crystals respectively, from the leach products.

The first stage leach in the Marikana Base Metals Refinery (BMR) is an oxidative leach at atmospheric pressure. Leaching takes place in five continuously stirred tank reactors (CSTR's) in series. In the current circuit configuration, oxygen is sparged to

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the first three tanks. The atmospheric leach has the dual purpose of liberating nickel from the matte, while simultaneously rejecting copper from solution via cementation and/or metathesis reactions, where copper from solution is exchanged with nickel from the alloy and nickel-sulphide phases in the matte. Plant experience and metal accounting show that the PGMs will deport similarly to copper during the 1st stage atmospheric leach. Currently, the exact precipitation mechanism of PGMs to form part of the 1st stage residue, is poorly understood. Precipitation of Rh, Ru and Ir can either be through electrochemical cementation/reduction or through hydrolyses as the pH increases throughout the train of five leach tanks.

From the atmospheric leaching section, the liquid product is further processed to produce NiSO_4 crystals. About 60% of the 1st stage residue from the atmospheric leach is recycled to the first CSTR, to increase Ni-extraction to approximately 80%, while the remainder of the solids are transferred to high pressure autoclaves, where copper sulphides and the remaining nickel sulphides are leached and some of the PGMs (Rh, Ru and Ir) enter the leach solution (Dorfling et al., 2010). From the high pressure leach liquor, copper cathodes are recovered in the copper electrowinning section after Se and Te removal. Spent electrolyte from the copper electrowinning tankhouse is recycled to the atmospheric leach and used as leaching agent in the first stage leach. This spent electrolyte contains a high concentration of sulphuric acid and dissolved copper (approximately 75 g/L and 35 g/L, respectively). The mineralogical transition of the matte leach residue as it progresses through the 1st stage leach is described below.

Previous research on the leaching behaviour of Ni–Cu–S mattes in a sulphuric acid leach was conducted by Lamya and Lorenzen (2006), Füglerberg et al. (1995), Hofirek and Kerfoot (1992), Symens et al. (1979) and Llanos et al. (1974). Although the major features of this process have been clarified by these authors, results on the effects of different initial acid and copper concentrations are sometimes contradicting or limited. Fundamental understanding of the mechanisms controlling the reaction kinetics is also limited, perhaps because different controlling mechanisms have been found to be operative depending on operating conditions (Lamya, 2007). Therefore, the prediction of the effects of changing operating variables on the overall process performance remains complex.

This paper reports the results from a well controlled experimental campaign to investigate the leaching of converter matte at atmospheric pressure. The roles of copper and acid concentrations on reaction kinetics, both under oxidative and non-oxidative conditions are investigated in detail. The non-oxidising leach is investigated to isolate the effect of the metathesis and cementation reactions. The understanding gained in these effects will serve as basis for the development of kinetic rate expressions in future work.

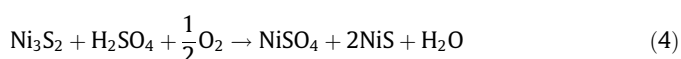
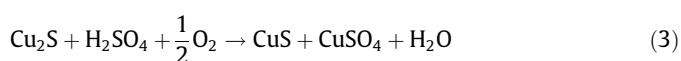
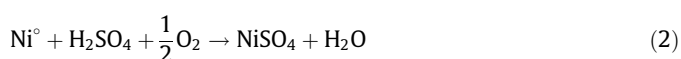
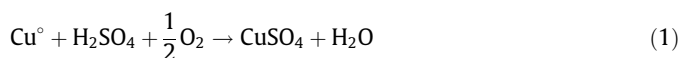
2. Theory

Burkin (2001) discusses the chemistry of industrial leaching processes and tabulates the typical operating conditions used in the extraction of Ni and Cu from converter mattes derived from the Ni-industry and the PGM industry. Ni-extraction in the PGM industry is performed both under atmospheric and pressure leach conditions, typically using anolyte/spent electrolyte of 70–100 g/L H_2SO_4 which is higher than traditional Ni matte leaching in the absence of PGM's.

The leaching chemistry of Ni–Cu–S mattes has been described and reviewed by several authors (Llanos et al., 1974; Hofirek and Kerfoot, 1992; Lamya and Lorenzen, 2006; Bryson et al., 2008). As leaching progresses, several reaction stages can be operative, depending on the solution pH, E_h , concentrations, and the

availability of reactants. During the early stages of the leach, the leaching of metal constituents by sulphuric acid are predominant, while iron and copper are removed from solution via hydrolysis as the pH increases. Different stages occurring during leaching are characterised by different sets of chemical reactions that take place in parallel. The most important reactions that are operative will be discussed.

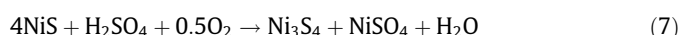
Copper and nickel in the matte were found to occur mainly in the sulphide phase, although significant amounts were also found in the Ni–Cu alloy phase, as shown in Table 3. In both instances leaching (at 85 °C and atmospheric pressure) occurs via reaction with oxygen and sulphuric acid:



Plasket and Romanchuk (1978) and Füglerberg et al. (1995) noted that the dissolution of millerite (NiS) can proceed under highly oxidising conditions Reaction (5). Plasket and Romanchuk (1978) also note the possible redissolution of copper under highly oxidising conditions during later stages of the leach (Reaction (6)):



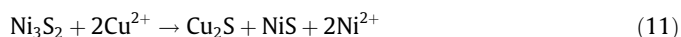
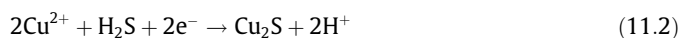
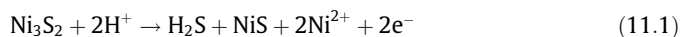
Füglerberg et al. (1995) further noted that millerite can be converted to polydymite (Ni_3S_4) under highly oxidative conditions (Reaction (7)), or react with copper in solution in an exchange reaction as given in Reaction (8).



Metathesis (Reactions (8) and (9)) and cementation (Reaction (10)) reactions, where copper from solution respectively exchanges with nickel in the nickel sulphide matrix or with nickel from the alloy, are responsible for removing copper from solution, while also dissolving nickel. These reactions occur simultaneously with leaching reactions (Reactions (1)–(4)).

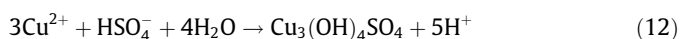


Rademan et al. (1999) explained the cementation reaction of copper with heazlewoodite as a two-step mechanism, occurring with hydrogen sulphide as an intermediate:

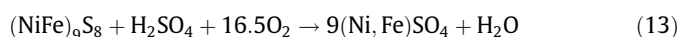


From the proposed mechanism, it follows that interaction might occur between copper and sulphuric acid during the leach and that the rate of cementation might be influenced by acid availability.

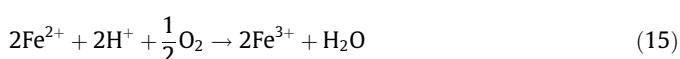
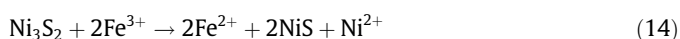
In the higher pH ranges (4.5–6), copper hydrolysis takes place, accompanied by the formation of basic cupric sulphate (antlerite) (Hofirek and Kerfoot, 1992):



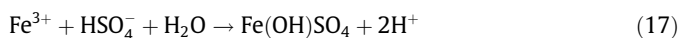
Iron was found to be present in the matte in the form of pentlandite ((NiFe)₉S₈). According to Knuutila et al. (1997), pentlandite reacts with sulphuric acid according to Reaction (13):



Although present in relatively small concentrations, iron has been reported to play an important role as catalyst and oxygen carrier to enhance the rates of leaching reactions (Burkin, 2001; Mulak, 1987; Hofirek and Kerfoot, 1992). Reactions (14) and (15) show how the ferric ion is reduced to the ferrous state in the leaching of heazlewoodite (Reaction (14)), and then reproduced when ferrous is oxidised to the ferric state by dissolved oxygen (Reaction (15)).



Reduction to the ferrous state ceases at pH values above 2–2.5 (Hofirek and Kerfoot, 1992). At pH values above 3.5, the ferric ion becomes unstable and the following hydrolysis reactions might take place:



3. Materials and methods

3.1. Materials

Spent electrolyte and granulated converter matte from the Lonmin Marikana BMR were used in this study. Spent electrolyte was diluted with water to obtain the desired initial concentrations and used as base for all tests. In the high copper and high acid tests, CuSO₄·5H₂O crystals and 98% H₂SO₄ were respectively used to increase initial copper and acid concentrations.

The matte was milled for 4 h in a rubber lined batch mill to obtain a size distribution similar to that used at the BMR (Table 1).

The chemical composition of the matte is shown in Table 2 and the relative phase abundances in wt% is given in Table 3, as determined by Quantitative XRD analysis.

Heazlewoodite was found to be the most abundant phase, constituting 53.8% of the matte. Nickel was also present in the form of godlevskite and pentlandite, a nickel–iron sulphide phase. Iron is present in magnetite and troilite with minimal relative abundances of 1.2% and 0.9% respectively. Magnetite is characteristically considered to be unreactive during leaching. Copper is predominantly present in chalcocite phases. A small amount was present in a cuprite phase, but was considered insignificant in leaching.

Table 1

Comparison of size distributions of matte from Lonmin Marikana BMR and laboratory milled matte.

Particle size (μm)	Particle size distribution (vol%)	
	Laboratory	Plant material
–200 + 100	10.7	10.5
–100 + 80	8.8	6.5
–80 + 60	11.9	10.6
–60 + 40	14.0	16.1
–40	54.3	56.2

Particle size distribution determined with Saturn Digisizer 5200 V1.10.

Table 2

Chemical composition of converter matte (XRF analysis).

Element	Abundance (wt%)
Ni	49.1
Cu	26.6
S	24.4
Co	0.5
Fe	0.9

Table 3

Relative phase abundances in wt% of converter matte (XRD analysis).

Mineral	Chemical formula	Abundance (wt%)
Chalcocite M	Cu ₂ S	10.4
Chalcocite T	Cu ₂ S	16.2
Cu–Ni alloy		12.3
Cuprite	Cu ₂ O	0.2
Godlevskite	Ni ₇ S ₆	4.4
Heazlewoodite	Ni ₃ S ₂	53.8
Magnetite	Fe ₃ O ₄	1.2
Pentlandite	(NiFe) ₉ S ₈	0.7
Troilite	FeS	0.9

A scanning electron microscope induced backscattered image at 20 μm scale is shown in Fig. 1 and reveal euhedral copper-sulphide (Cc) phases and anhedral nickel-sulphide phases (Hw). Copper and nickel is also present in nickel–copper alloy phase (Al) generally characteristic of varying morphologies and nickel:copper ratios. The nickel-sulphide phases appear to form a cementing matrix embedding the available copper-sulphide and nickel–copper alloy phases. Furthermore, the alloy phases appear to act as prime collectors for the platinum-group metals and are generally manifested by the presence of a platinum enriched core. Results for spot analysis of particularly the alloy phase and the PGM containing core are given in Table 4.

3.2. Equipment

Experiments were conducted in a 5 L glass stirred batch reactor. The reactor was equipped with a band heater with PLC controller to control the temperature between 84 °C and 86 °C. A manually operated cooling coil was available to remove excess heat. The reactor was covered and equipped with a condenser to minimise evaporation. Oxygen was sparged into the reactor during oxidative tests, while nitrogen was sparged into the vessel during non-oxidative tests.

The laboratory reactor was geometrically similar to reactors at Lonmin Marikana, to simulate hydrodynamic conditions. The stirring rate was scaled in order to obtain equal solids suspension in the laboratory reactor. A comparison of the laboratory and plant reactor geometries is given in Table 5.

3.3. Experimental procedure

After filling the reactor with the initial leach solution, stirring was started and the temperature was increased to 85 °C. The nitrogen or oxygen was fed to the reactor continuously, starting approximately 40 min prior to leaching. When the reactor had stabilised at the correct temperature, the milled matte was fed through a port in the reactor cover. This was taken as time zero.

A pipette was used to periodically take 15 ml samples from the reactor. Samples were filtered to remove all particles larger than 0.2 μm in order to prevent further reaction and the pH of the liquid samples were noted.

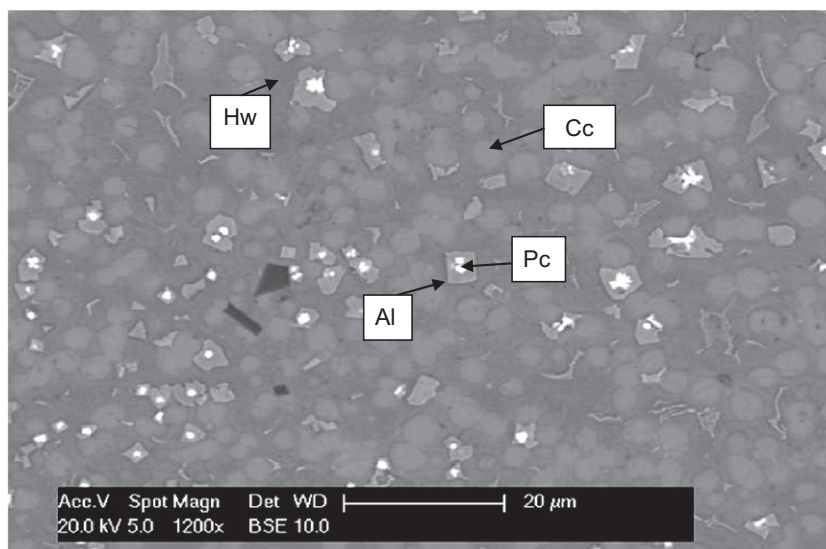


Fig. 1. Backscattered electron image indicating phases occurring. Various points were analysed on a particle of converter matte and compositions of the indicated phases are given in Table 4. Hw = heazlewoodite, Cc = chalcocite, Al = alloy, Pc = PGM alloy inclusion.

Table 4

Chemical composition of mineral phases shown in Fig. 1.

Pos.	O	S	Fe	Co	Ni	Cu	Ru	Rh	Pd	Os	Ir	Pt
Al _{wt%}		1.96	0.44	1.12	75.19	21.28						
Pc _{wt%}		0.54	0.49	0.88	41.79	25.86		0.71				29.73

Table 5

Comparison of laboratory and plant reactor geometries.

	Plant	Laboratory batch reactor
Number of baffles	4	4
L (mm)	2600	160
Di (mm)	1150	92
D (mm)	2865	190
L/D	0.908	0.842
Di/D	0.401	0.484
Oxygen flowrate (L/min)	833	0.20
Reactor volume (L)	16,761	4.30
Oxygen flow/volume (L/min/L)	0.05	0.05
Stirring rate (rpm)	88	1100

The final pulp was filtered in a pressure filter and the filter cake washed with distilled water. The solid residue was dried at approximately 45 °C, weighed and sampled for chemical and mineralogical analysis.

3.4. Chemical analysis

Liquid samples were analysed for Cu, Ni, Co and Fe concentration, using inductively coupled plasma (Varian Radial ICP-AES). XRF analyses of solid samples were performed with a Panalytical

AXIOS 2.4 kW instrument fitted with a Rh X-ray tube, to determine the Cu, Ni, Fe, S and Co content. To determine the mineralogy of leach residues, XRD analysis of solid samples were done using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector. X'Pert Highscore Plus software was used to identify the phases.

3.5. Experimental conditions

Leaching experiments were conducted with diluted spent electrolyte from the Lonmin Marikana BMR. The approach in the experiments was to vary the initial acid concentration, the initial copper concentration and the gas fed to the reactor, while all other variables were kept constant. Fixed test conditions are given in Table 6, while variable conditions are indicated in Table 7.

The solids/liquids ratio was determined so that the combined molar quantity of dissolved copper and acid in the leach solution always exceeded the moles of nickel in the matte, making complete rejection of copper and acid impossible. This approach was followed in order to determine how the kinetics of leaching would change as leaching progressed, considering that reactants in solution would not become limiting.

Table 6

Fixed conditions used in laboratory batch tests.

Test condition	Value
Temperature	85 °C
Stirring rate	1100 rpm
Oxygen/nitrogen flowrate	0.2 L/min
Initial concentrations	
Fe concentration	365 ppm
Ni concentration	31 g/L
Solids content	81 g solids/L solution
Liquid density	1190 g/L

Table 7
Experimental conditions employed in batch leaching tests.

Experiment no.	Initial Cu concentration (g/L)	Initial acid concentration (g/L)	Gas feed
1	37	37	Nitrogen
2	37	37	Oxygen
3	18	37	Nitrogen
4	18	37	Oxygen
5	37	74	Nitrogen
6	37	74	Oxygen
8	18	74	Oxygen

4. Results and discussion

4.1. Comparison of metal extractions obtained in oxidative and non-oxidative tests

Table 8 summarises the extractions obtained after 240 min. The mineralogy of the leach residues that were obtained are given in Table 9. On the plant, 80% of the nickel is typically extracted in the first stage leach, while the rest is extracted during pressure leaching. The lower extractions obtained in laboratory work can be attributed to the recycle stream which is employed on the plant but which was not simulated on batch scale.

By comparing extractions and the mineralogy of residues from different tests, it can be seen that oxygen availability was the most important factor influencing leaching. When comparing oxidative and non-oxidative tests with identical initial concentrations (Run 1 and 2, Run 3 and 4, Run 5 and 6, respectively), it can be seen that lower nickel and iron extractions were obtained during non-oxidative leaching, due to the suppression of acid–oxygen leaching reactions (Reactions 2, 4, and 13).

Rademan et al. (1999) showed that the leaching of nickel and copper sulphides proceed through the formation of several intermediates in which the sulphur:metal ratio increases as leaching progresses. Based on X-ray powder diffraction, Burkin (2001) gives a mineralogical progression in agreement to that of Rademan et al. (1999).

For Cu sulphides the following sequence was suggested:

Chalcocite ($\text{Cu}_{1.993}\text{S}$ – Cu_2S) \Rightarrow Djurleite ($\text{Cu}_{1.934}\text{S}$ – $\text{Cu}_{1.965}\text{S}$) \Rightarrow Digenite ($\text{Cu}_{1.765}\text{S}$ – $\text{Cu}_{1.79}\text{S}$) below 83 °C or high Digenite

Table 8
Metal extractions obtained in batch leaching tests (the corresponding test conditions are given in Tables 6 and 7).

Experiment	Metal extraction into solution			
	Nickel (mass%)	Fe (mass%)	Cu (% removed) ^a	Cu (% extracted)
<i>Oxidising tests</i>				
2. Low acid. High Cu	61.9	Hydrolysed	20.2	n/a
4. Low acid. Low Cu	59.1	Hydrolysed	39.5	n/a
6. High acid. High Cu	61.0	89.8	n/a	45.9
8. High acid. Low Cu	63.4	97.1	n/a	46.3
<i>Non-oxidising tests</i>				
1. Low acid. High Cu	22.3	85.7	12.5	n/a
3. Low acid. Low Cu	22.2	84.6	26.0	n/a
5. High acid. High Cu	21.7	82.5	13.3	n/a

^a Copper removed from liquid to solid phase – determined from ICP-AES analysis of liquid samples. All other values were determined by comparing initial and final solid material masses and compositions (XRF).

($\text{Cu}_{1.8}\text{S}$ – $\text{Cu}_{1.83}\text{S}$) above 83 °C \Rightarrow Blaubleinder Covellite ($\text{Cu}_{1.05}\text{S}$ – $\text{Cu}_{1.10}\text{S}$) or ($\text{Cu}_{1.05}\text{S}$ – $\text{Cu}_{1.4}\text{S}$), finally to Covellite (CuS), of which its complex crystallographic structure is belied by its apparent simple stoichiometry.

Nickel sulphides are similarly becoming metal-depleted as leaching progresses from Heazlewoodite (Ni_3S_2) \Rightarrow Millerite (NiS) \Rightarrow Polydymite (Ni_3S_4).

In the presence of Cu and Fe, lattice substitution may lead to solid solution and variable stoichiometry minerals, e.g. where Ni partially replaces Cu in djurleite.

The leaching residues obtained in non-oxidative tests (Run 1, 3 and 5) were very similar to the starting material, with heazlewoodite (Ni_3S_2) and chalcocite (Cu_2S) making out the major phases. During oxidative leaching (Run 2, 4, 6 and 8), reactions proceeded further so that the major phases present were millerite (NiS) and covellite (CuS).

When comparing copper removal for Run 1 and 2, Run 3 and 4 and Run 5 and 6 respectively, it can be seen that the amount of copper rejected from solution was higher in oxidative tests, except when the acid concentration was high enough to lead to copper leaching (Run 6 and Run 8). The increased copper removal during oxidative leaching can be attributed to some extent to copper hydrolysis (Reaction (12)) and the formation of antlerite. The effect of oxygen on the rate of the cementation reaction is therefore not immediately clear.

The effects of initial acid and copper concentrations will be discussed in more detail under following headings. In general, non-oxidative results were found to be less sensitive to changes in the initial acid concentration than oxidative tests. In both oxidative and non-oxidative tests, the results were relatively insensitive to the initial copper concentration.

4.2. Oxidising leach tests

4.2.1. Oxidative reaction mechanisms

Results for Run 2 (oxidising leach, initial concentrations: 37 g/L copper, 37 g/L acid) are shown in Fig. 2. Only Run 2 from the oxidative tests will be fully discussed. Deviations which occurred due to different initial concentrations in Run 4, 6 and 8 will be discussed under the next heading.

In order to ease discussion of the leaching test, five stages will be identified to highlight specific features of Fig. 2.

4.2.1.1. Stage 1: 0–15 min (pH ~1). Nickel and iron extraction were fast during the first 15 min of the test. Respectively 30% (mass) of the nickel and 85% of the iron initially present in the matte was leached in this period. Copper cementation did not take place, indicating that nickel dissolution occurred via reaction with sulphuric acid (Reactions (2) and (4)). Many authors have indicated that the alloy phase is the most reactive (Lamya and Lorenzen, 2006; Provis et al., 2003; Dutrizac and Chen, 1987) and the fast initial nickel extraction was likely via leaching from the alloy phase (Reaction (2)). Iron extraction was probably due to the leaching of pentlandite (Reaction (13)).

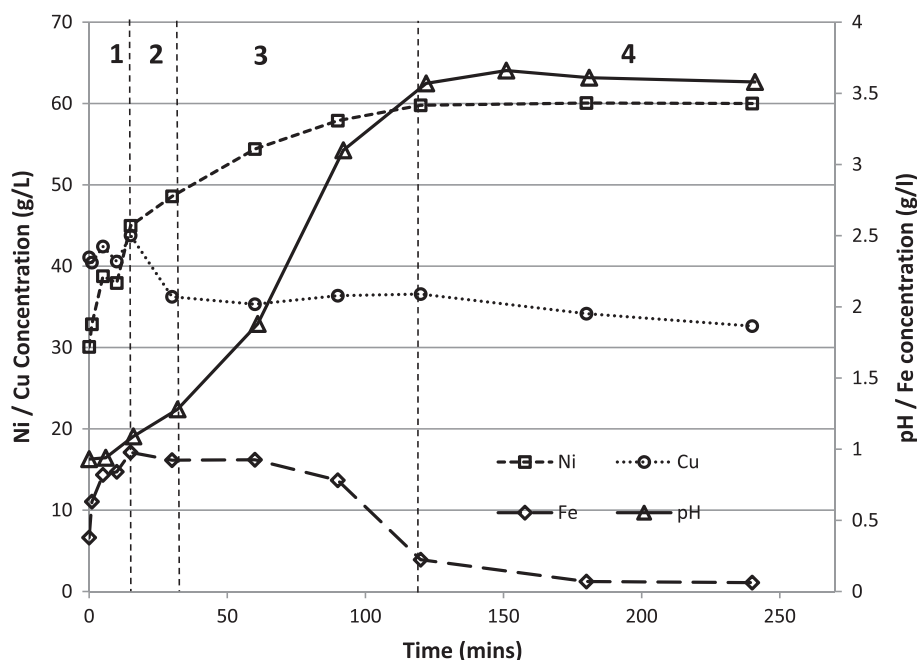
4.2.1.2. Stage 2: 15–30 min (pH 1–1.3). After 15 min most of the available iron had been leached from the matte and iron dissolution ceased.

Cementation occurred between 15 and 30 min, but came to a stop after this period, despite the fact that 70% of the nickel in the matte was unleached at this stage. One explanation would be that copper removal occurred preferentially via reaction with the alloy phase, rather than via reaction with the nickel sulphide phase. Copper removal then ceased once the nickel in the alloy phase was depleted. A second possible explanation is that copper cementation onto heazlewoodite did initially take place, but that

Table 9

Mineral composition (XRD analysis) of starting material and leach residues from batch leaching tests (test conditions given in Tables 6 and 7).

Mineral		Starting material Mass%	Non-oxidative test residues			Oxidative test residues ^b		
			Run 1 ^a (+ –) Mass%	Run 3 ^a (– –) Mass%	Run 5 ^a (+ +) Mass%	Run 2 ^a (+ –) Mass%	Run 6 ^a (+ +) Mass%	Run 8 ^a (– +) Mass%
Heazlewoodite	Ni ₃ S ₂	53.78	51.02	51.39	51.45		3.08	4.09
Chalcocite M	Cu ₂ S	10.39	13.52	13.61	14.07			
Chalcocite T	Cu ₂ S	16.19	21.24	21.08	21.28			
Cu–Ni		12.34	8.7	8.81	8.11			
Cuprite	Cu ₂ O	0.17	0.94	0.87	0.88			
Godlevskite	Ni ₇ S ₆	4.43	3.11	3.22	3.03			
Magnetite	Fe ₃ O ₄	1.18	0.1	0	0.1			
Pentlandite	(NiFe) ₉ S ₈	0.67	0.56	0.36	0.45			
Troilite	FeS	0.88	0.81	0.66	0.61			
Millerite	NiS		–	–	–	35.39	52.49	51.29
Polydymite	Ni ₃ S ₄						13.68	11.58
Covellite	CuS		–	–	–	16.3	30.75	33.04
Digenite	Cu ₉ S ₅		–	–	–	9.23		
Malachite	Cu ₂ CO ₃ (OH) ₂		–	–	–	8.57		
Antlerite	Cu ₃ SO ₄ (OH) ₄		–	–	–	30.51		

^a (Cu, acid). Cu: '–' = 18 g/L, '+' = 37 g/L. Acid: '–' = 37 g/L, '+' = 74 g/L.^b XRD results for Run 4 not available.**Fig. 2.** Concentration and pH changes during Run 2 (oxidative leach. 37 g/L Cu, 37 g/L acid), indicating different stages during leaching. Note that iron concentration and pH are indicated on the secondary axis. Stage 1: 0–15 min, pH ~1. Stage 2: 15–30 min, pH 1–1.3. Stage 3: 30–120 min, pH 1.3–3.6. Stage 4: 120–240 min, pH 3.6.

the formation of a solid reaction product layer from Reaction (11) (Cu₂S) inhibited further reaction.

4.2.1.3. Stage 3: 30–120 min (pH 1.3–3.6). In the period from 30 to 120 min nickel is leached out of the sulphide matrix and millerite is formed according to Reaction (4). Copper did not react during this period. Iron was hydrolysed out of solution between 60 and 180 min (Reactions (17) and (18)).

4.2.1.4. Stage 4: 120–240 min (pH 3.6). After 120 min, almost all the iron is hydrolysed out of solution and copper hydrolysis commences. Mineralogical analysis of the leach residue confirmed the formation of antlerite (Cu₃(OH)₄SO₄), according to Reaction (12). The hydrolysis reaction produces acid, which explains the plateau in the pH after 120 min. Nickel dissolution ceased at a

pH of 3.6, with approximately 60 mass% nickel extraction. Nickel dissolution was assumed to have stopped due to the combined effects of low acid and iron concentrations (leading to slower oxidation reactions (Reactions (16) and (17))) and limited availability of leachable nickel.

4.2.2. Effect of initial acid concentration on oxidative leaching

Results from Run 2 (37 g/L copper, 37 g/L acid) and Run 6 (37 g/L copper, 74 g/L acid) are compared in Fig. 3 to demonstrate the effect of acid on oxidative leaching. Similar effects to those shown in Fig. 3 were observed when comparing Run 4 (18 g/L copper, 37 g/L acid) with Run 8 (18 g/L copper, 74 g/L acid).

In the high acid run (Run 6), acid was available for leaching throughout the test and only a slight increase in the pH is visible (Fig. 3a). The increased availability of acid in Run 6 did not

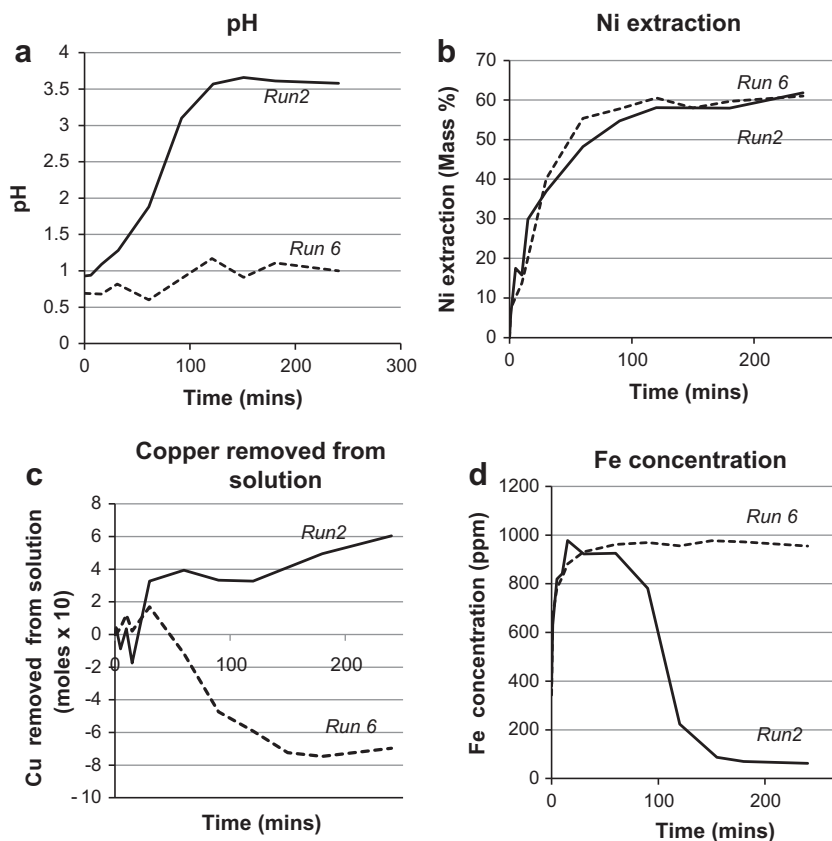


Fig. 3. Comparison of results from Run 2 (solid line) (37 g/L copper, 37 g/L acid) and Run 6 (broken line) (37 g/L copper, 74 g/L acid), to demonstrate the effect of the initial acid concentration on leaching.

influence nickel extraction by Reactions (2) and (4) (Fig. 3b), but XRD results show that the leaching conditions in high acid runs were suitable for the conversion of millerite (NiS) to polydymite (Ni_3S_4) (Reaction (7)). No polydymite was found in the residues from low acid runs.

No cementation occurred in high acid runs and very little in low acid runs (Fig. 3c). Hofirek and Kerfoot (1992) characterised different modes of Ni–Cu–S converter matte leaching at 80 °C, based on the initial acid concentration. Systems with moderate or high acid solutions (acid concentration > 10 g/L, acid/matte ratio > 0.1 weight/weight) were distinguished by total copper rejection during cementation, followed by iron hydrolysis.

In the current work, it was found that copper was leached out of the matte faster than it was removed from solution in the high acid run (Run 6). In low acid runs, copper was partly removed from solution, but the presence of digenite (Cu_9S_5) in the residue from Run 2 indicates that leaching of Cu_2S had taken place to some extent in the low acid runs as well. Copper removal in low acid runs was also only partly due to cementation, while hydrolysis (supported by the formation of antlerite – Table 9) was in part responsible for copper removal.

Symens et al. (1979) investigated the leaching of Ni–Cu–S mattes with a sulphuric acid/copper solution and found that highly oxidative conditions can interfere with copper removal via cementation. Plasket and Romanchuk (1978) reported similar results. At initial concentrations of 20 g/L Cu, 25 g/L Ni and 60–120 g/L acid, with a leaching temperature of 132 °C, it was found that the leach had to be carried out with no oxygen added towards the end of the leach in order to prevent the dissolution of CuS (Reaction (6)). The current work supports these findings and show that an excess of oxygen and acid interferes with copper cementation. The high

stirring rate employed in the current work (1100 rpm) might have contributed to high oxygen transfer rates and consequently to copper leaching in the high acid runs.

Copper leaching only occurred a few minutes after leaching had started. It is possible that chalcocite was only exposed to leaching after a period of Ni-leaching lead to pore formation in the heazlewoodite matrix.

Fig. 3d shows that no iron hydrolysis took place in high acid runs. Similar iron extractions were obtained in the high and low acid tests (~90%), before iron hydrolysis took place, indicating that all the available iron had been leached.

4.2.3. Effect of initial copper concentration on oxidative leaching

Results from Run 2 (37 g/L copper, 37 g/L acid) and Run 4 (18 g/L copper, 37 g/L acid) are compared in Fig. 4 to demonstrate the effect of initial copper concentration on oxidative leaching. Similar effects were observed when comparing Run 6 (37 g/L copper, 74 g/L acid) with Run 8 (18 g/L copper, 74 g/L acid). Therefore only Run 2 and Run 4 will be discussed.

Llanos et al. (1974) noted that final nickel extraction was more sensitive to the sulphuric acid concentration than to initial copper concentration in the leach liquor. Results obtained in this study indicate that the effects of the initial copper concentration were generally less pronounced than the effect of the initial acid concentration (especially with reference to the behaviour of iron and copper), but that neither variable had a significant influence on nickel extraction.

Fig. 4a shows a quicker rise in the pH at a lower initial copper concentration (Run 4) which coincided with a slight increase in the rate of nickel dissolution (Fig. 4b). This might suggest a slight change in the leaching behaviour of nickel due to changes in the

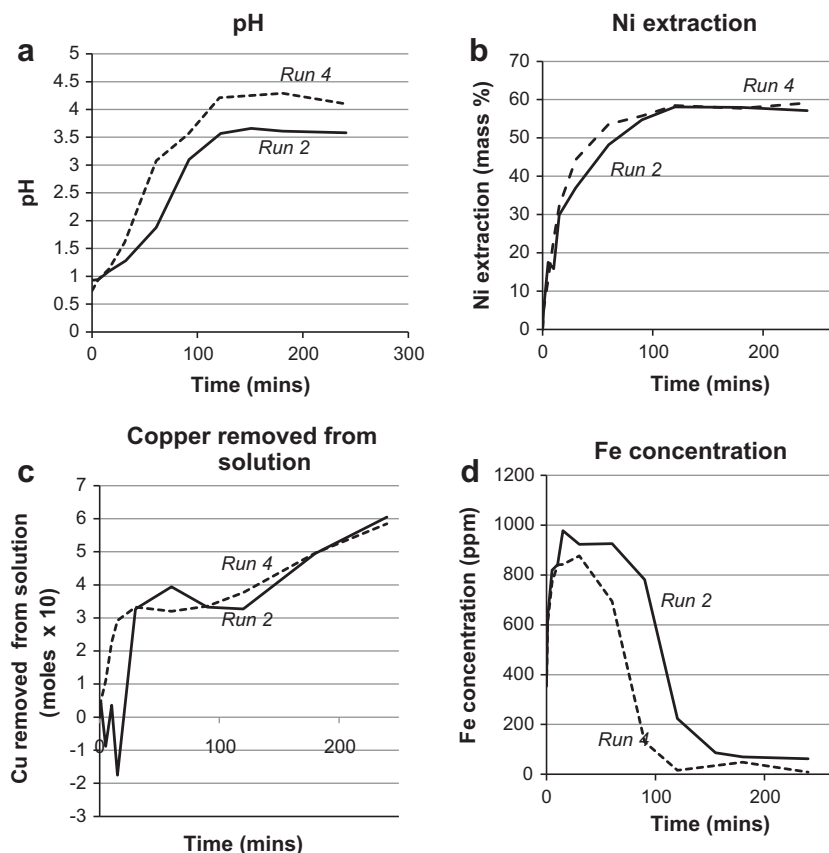


Fig. 4. Comparison of results from Run 2 (solid line) (37 g/L copper, 37 g/L acid) and Run 4 (broken line) (18 g/L copper, 37 g/L acid), to demonstrate the effects of the initial copper concentration on leaching.

copper concentration. The faster rise in solution pH was accompanied by an earlier onset of iron hydrolysis in Run 4 (Fig. 4d).

Fig. 4c shows that the initial rate of cementation was slower in the high copper run (Run 2), but that the same number of moles of copper was removed from solution in Run 2 and Run 4 (resulting in 20.2% copper removed in Run 2 and 39.5% copper removed in Run 4).

Lamya (2007) investigated the non-oxidative leaching of Ni-Cu-S matte and found that the rate of cementation decreased when the initial copper concentration was increased in the range of 25–48 g/L. This was attributed to changes in activity brought on by increased copper ion concentration, a higher solution viscosity and decreased copper ion diffusivity at increased copper concentrations.

4.3. Non-oxidising leaching tests

4.3.1. Non-oxidative reaction mechanisms

The results obtained in non-oxidative leach tests were very similar from one run to the next, with smaller deviations occurring than in oxidising tests. Results for Run 3 (non-oxidative, 18 g/L Cu, 37 g/L acid) are shown in Fig. 5.

Nickel extractions were much smaller in non-oxidative tests (~20%) than in oxidative tests (~60%). Nickel was mostly liberated by exchange reactions with copper (Reactions (9) and (10)), but a stoichiometric analysis of results show that approximately 1.6 moles nickel was extracted for every mole copper cemented, indicating that an acid-leaching reaction (Reaction (18)) was operative in the absence of oxygen.



Fig. 5 shows that very little acid was consumed by leaching and only small changes occurred in the pH.

Copper cementation was initially rapid, but slowed down after 10 min. Ni-Cu alloy was still present in the solid residues from non-oxidative tests, indicating that the rate of cementation was not limited by the available alloy in the matte. Mackinnon (1974) investigated the recovery of copper by cementation onto nickel powder and noticed that a passivating product layer could inhibit reactions. Annamalai and Murr (1979) investigated the cementation of copper onto a rotating iron disk and found that a smooth copper deposit formed at high rotation rates, which inhibited reaction rates, whereas a rate-enhancing dendritic deposit formed at lower rotation rates. It is possible that a rate-limiting product layer could have formed under the current experimental conditions (low solids/liquid ratio and high agitation rate), although this cannot be confirmed without further characterisation of the leach residue.

Iron was dissolved quickly within the first 15 min of the leach. During this period some dissolved oxygen was probably still available in the leach solution for leaching reactions to take place (Reaction (13)), although nitrogen was sparged into the solution. Iron was also seen to leach out in a two-step mechanism, with leaching reactions slowing down at around the same time as copper cementation slowed down. Changes in the mineralogy and structure of the matte might give an explanation for the changing reaction rates.

4.3.2. Effects of initial acid on non-oxidative leach

Results from Run 1 (37 g/L copper, 37 g/L acid) are compared with results from Run 5 (37 g/L copper, 74 g/L acid) in Fig. 6, to demonstrate the effect of the initial acid concentration on the non-oxidative leach.

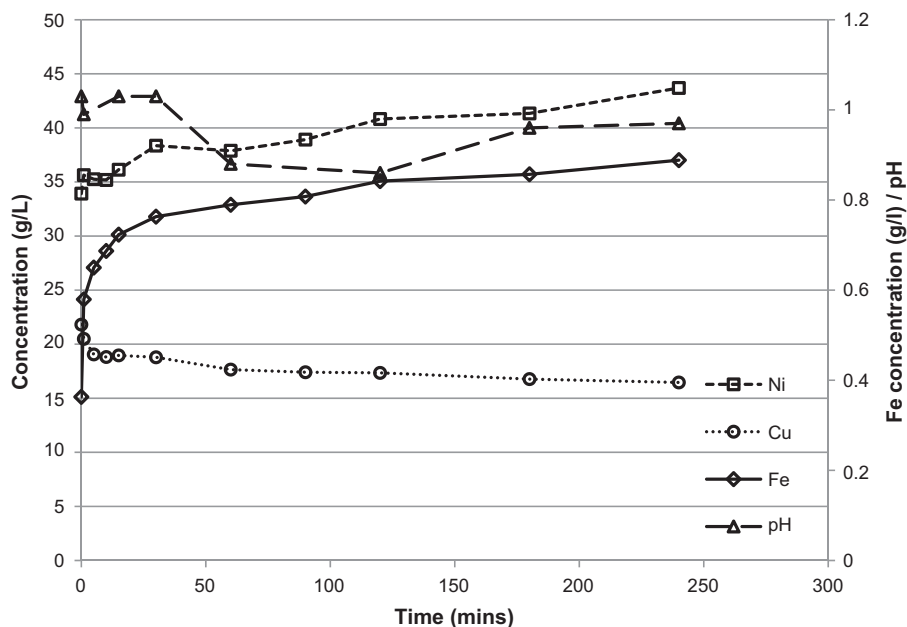


Fig. 5. Concentration and pH changes during Run 3. (Non-oxidative leach. Initial concentrations: 18 g/L Cu; 37 g/L acid. Note that the iron concentration and pH are indicated on the secondary axis.)

Most reactions involving acid are oxygen dependent and therefore the initial acid concentration had little influence on non-oxidative leaching. Fig. 6a shows that the behaviour of nickel was similar in the high acid (Run 5) and low acid (Run 1) tests. Similarly, the behaviour of iron was the same for both tests

(Fig. 6c). The fast initial leaching rates of nickel and iron was attributed to dissolved oxygen or Fe^{3+} ions which were present in the system at the start of tests.

Fig. 6b shows the effect of acid concentration on cementation kinetics. Hofirek and Kerfoot (1992) previously noted that

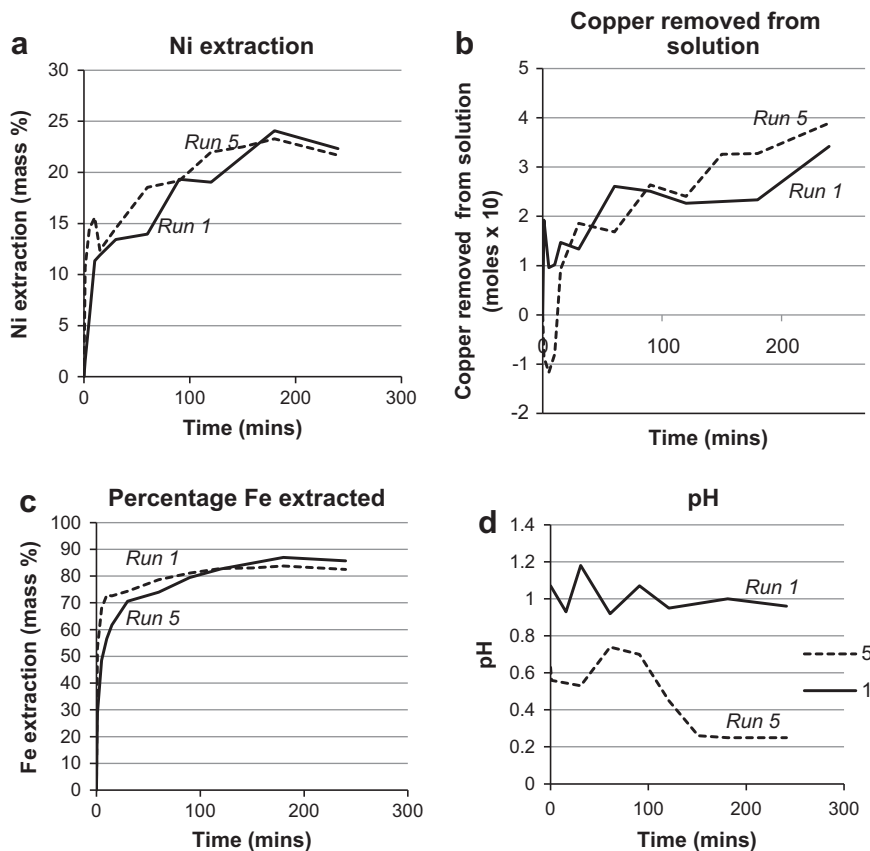


Fig. 6. Comparison of results from Run 1 (solid line) (37 g/L copper, 37 g/L acid) and Run 5 (broken line) (37 g/L copper, 74 g/L acid), to demonstrate the effects of the initial acid concentration on non-oxidative leaching.

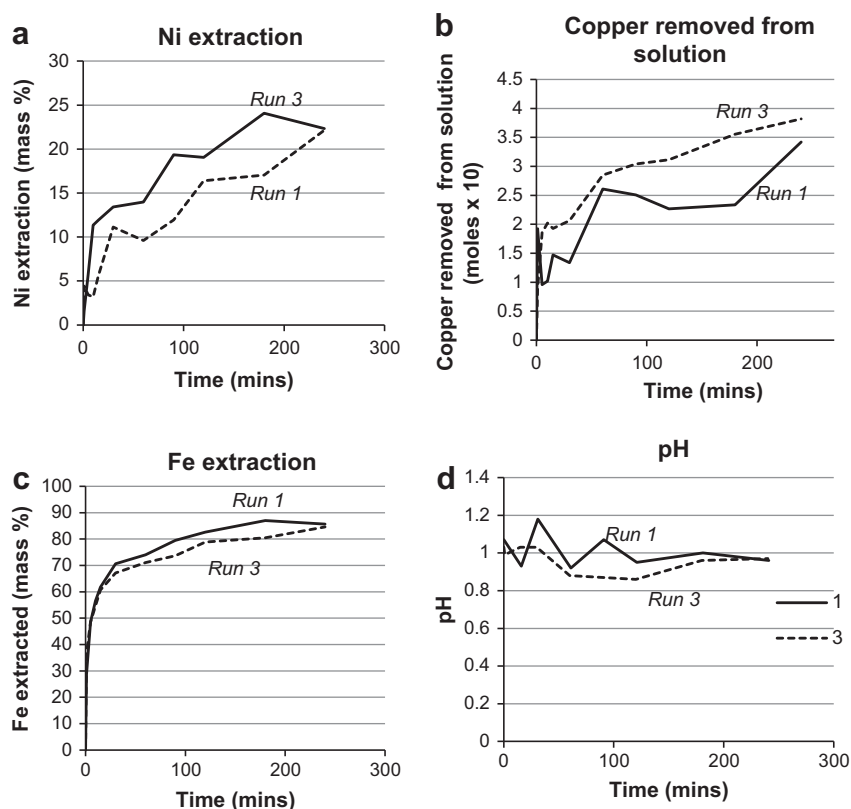


Fig. 7. Comparison of results from Run 1 (solid line) (37 g/L copper, 37 g/L acid) and Run 3 (broken line) (18 g/L copper, 37 g/L acid), to demonstrate the effects of the initial copper concentration on non-oxidative leaching.

cementation only proceeds in the presence of hydrogen ions and accelerates with increasing acid concentration. Symens et al. (1979) also noted an increase in cementation rates when increasing the $\text{H}_2\text{SO}_4/\text{Cu}^{2+}$ ratio. It can be seen that copper was initially leached out of the matte in Run 5 (high acid), but once cementation started, the rate of the reaction was faster than for Run 1 (low acid). This might be attributed to increased porosity and reaction area due to the initial leaching reaction in the high acid run.

4.3.3. Effect of initial copper concentration on non-oxidative leaching

Results from Run 1 (37 g/L copper, 37 g/L acid) and Run 3 (18 g/L copper, 37 g/L acid) are compared in Fig. 7. Lamy (2007) previously found that metal extractions were not significantly influenced by the initial copper concentration, but that the rate of cementation decreased at higher concentrations. The current work shows that the copper concentration did not have a significant effect on metal extractions or reaction rates, although the rate of cementation seemed to increase slightly at a lower copper concentration (Run 3).

5. Conclusions

Batch leaching tests were conducted to investigate the effect of three variables on the leaching of Ni–Cu–S Peirce Smith converter matte. The initial acid and copper concentrations were varied for respectively oxidative and non-oxidative leaching. The purpose of the work was to improve understanding of controlling mechanisms and to serve as basis for the development of kinetic rate expressions in future work.

Major differences were observed between the mechanisms operative during oxidative and non-oxidative leaching, specifically with reference to the utilisation of acid, which was much higher in

oxidative runs. Iron and copper hydrolysis only occurred during oxidative leaching, where the pH rose significantly during leaching.

Oxidative leaching was found to yield higher nickel extractions than non-oxidative leaching (~60% and ~20%, respectively), as well as higher rates of nickel extraction. This indicated that the kinetics of acid leaching were faster than the kinetics of cementation and metathesis reactions.

In terms of copper removal via cementation or metathesis, it was originally thought that the availability of oxygen might not have a significant influence, other than the fact that oxygen–acid-leaching reactions would compete for the available nickel in the matte. However, it was found that the key difference between oxidative and non-oxidative leaching was not a change in the rate of the cementation or metathesis reactions, but rather a change in the rate of copper leaching from chalcocite to produce covellite. In oxidative runs with a high initial acid concentration, copper was leached out of the matte to a larger extent than it was removed from solution, with 46% copper extracted from the matte, but even in oxidative experiments with low initial acid concentrations, a large amount of covellite in the residue indicated that copper leaching did take place. In low acid runs, copper removal from solution was largely as a result of hydrolysis. Highly oxidative conditions can therefore lead to increased copper leaching rates and interfere with complete copper removal via cementation or metathesis.

During non-oxidative leaching, the extent and rate of copper removal was low despite the fact that copper leaching did not take place, indicating that the cementation rate was low due to another constraint, possibly a combination of effects of the pulp density and stirring rate employed in this work.

The initial copper concentration had very little influence on oxidative or non-oxidative leaching. The initial acid concentration strongly influenced the reaction mechanisms operative during

oxidative leaching with hydrolysis reactions only occurring when the initial acid concentration was sufficiently low for the pH changes during leaching to be significant. In terms of nickel extraction, the initial acid concentration did not have a significant influence, which suggests that operating at higher acid concentrations might interfere with copper removal, with no benefit in terms of nickel extraction.

Future work might include experimental work at higher pulp densities to investigate whether copper removal can be improved, as well as an investigation into mineralogical and physical changes occurring in solids during leaching, to determine whether slow cementation rates might be attributed to changes in the solid phase.

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