Minerals Engineering 24 (2011) 524–534

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

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

R.F. van Schalkwyk [a], J.J. Eksteen [b,*], J. Petersen [c], E.L. Thyse [a], G. Akdogan [a]

[a] Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa
[b] Lonmin, Western Platinum, Process Division, Private Bag X508, Marikana 0284, South Africa
[c] Department of Chemical Engineering, University of Cape Town, Private Bag X3, Rondebosch 7701, South Africa

ARTICLE INFO

Article history:
Available online 20 November 2010

Keywords:
Hydrometallurgy
Leaching
Sulphide ores
Cementation

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.

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 (Ni_3S_2), chalcocite (Cu_2S), 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 $NiSO_4{\cdot}6H_2O$ 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

---

* Corresponding author. Tel.: +27 823766055; fax: +27 115161310.
E-mail address: Jacques.Eksteen@lonmin.com (J.J. Eksteen).

0892-6875/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.mineng.2010.10.012

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), Fügleberg 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:

$$Cu^\circ + H_2SO_4 + \frac{1}{2}O_2 \rightarrow CuSO_4 + H_2O \tag{1}$$

$$Ni^\circ + H_2SO_4 + \frac{1}{2}O_2 \rightarrow NiSO_4 + H_2O \tag{2}$$

$$Cu_2S + H_2SO_4 + \frac{1}{2}O_2 \rightarrow CuS + CuSO_4 + H_2O \tag{3}$$

$$Ni_3S_2 + H_2SO_4 + \frac{1}{2}O_2 \rightarrow NiSO_4 + 2NiS + H_2O \tag{4}$$

Plasket and Romanchuk (1978) and Fügleberg 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)):

$$NiS + O_2 \rightarrow NiSO_4 \tag{5}$$

$$CuS + 2O_2 \rightarrow CuSO_4 \tag{6}$$

Fügleberg 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).

$$4NiS + H_2SO_4 + 0.5O_2 \rightarrow Ni_3S_4 + NiSO_4 + H_2O \tag{7}$$

$$NiS + Cu^{2+} \rightarrow CuS + Ni^{2+} \tag{8}$$

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)).

$$Ni_3S_2 + 2Cu^{2+} \rightarrow Cu_2S + NiS + 2Ni^{2+} \tag{9}$$

$$Ni^\circ + CuSO_4 \rightarrow NiSO_4 + Cu^\circ \tag{10}$$

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

$$Ni_3S_2 + 2H^+ \rightarrow H_2S + NiS + 2Ni^{2+} + 2e^- \tag{11.1}$$

$$2Cu^{2+} + H_2S + 2e^- \rightarrow Cu_2S + 2H^+ \tag{11.2}$$

$$Ni_3S_2 + 2Cu^{2+} \rightarrow Cu_2S + NiS + 2Ni^{2+} \tag{11}$$

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):