Determination of the relative leaching kinetics of Cu, Rh, Ru and Ir during the sulphuric acid pressure leaching of leach residue derived from Ni–Cu converter matte enriched in platinum group metals

C. Dorfling [a], G. Akdogan [a], S.M. Bradshaw [a], J.J. Eksteen [b,*]

[a] Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa
[b] Western Platinum Ltd., (Lonmin Plc), Marikana, South Africa

ABSTRACT

Hydrometallurgical process routes are typically used for separation of platinum group metals (PGMs) from base metals in Ni–Cu converter matte. Nickel dissolution is primarily achieved in the first stage leach (high pressure or atmospheric leaching, or a combination of the two), which is followed by second stage high pressure sulphuric acid/oxygen leaching to dissolve copper and the remaining nickel. PGMs are recovered from the leaching residue, and their dissolution must hence be limited. The leaching of base metals in the first stage has been characterised, but there is a limited understanding of the behaviour of metals, and more specifically PGMs, in the second stage pressure leach. This research presents the results of laboratory work performed to investigate the kinetics of leaching in the second stage pressure leach. The influence of key operating parameters such as the temperature, pressure, and initial acid concentration on PGM dissolution was investigated.

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1. Introduction

The second stage leach plays an important role in the hydrometallurgical process route used for the recovery of platinum group metals (PGMs) from nickel–copper matte. After dissolution of nickel and cementation of copper in the first stage leach, the solid residue is sent to the second stage leach where the primary objective is to dissolve copper as well as any remaining nickel and cobalt. To achieve this objective, second stage pressure leaching is typically performed in an acidic oxidative leaching environment at temperatures up to 150 °C and pressures up to 10 bar. At optimal operating conditions, maximum dissolution of copper and any remaining nickel should occur while the PGMs should remain in the solid phase to be recovered in downstream batch leaching steps.

In general, the kinetics of the second stage leaching process is poorly understood because of the complex nature of the leaching chemistry and the diverse mineralogy of the first stage residue to be leached. As a result, these processes are seldom operated at the optimal leaching conditions. Although several studies have investigated the behaviour of base metals in different leaching environments, there is very little information available about the dissolution and behaviour of PGMs under high pressure leaching conditions. The objective of this study is to investigate the effects that key operating variables have on the leaching kinetics of base metals and PGMs in a high pressure sulphuric acid/oxygen leaching system.

1.1. Leaching chemistry

Various studies have been performed to investigate the leaching chemistry of base metals from converter matte in the first stage leach (Lamya and Lorenzen, 2006; Rademan et al., 1999; Hofirek and Kerfoot, 1992). The chemistry of metal dissolution from the first stage residue in the second stage pressure leaching step is, however, of particular interest to this study.

Rademan et al. (1999) identified the dominant copper phases present in the first stage leach residue to be digenite ($Cu_{1.8}S$) and covellite (CuS), while nickel is typically present as millerite (NiS) and polydymite (Ni_3S_4). Comparable results were reported by Dorfling et al. (2010), who performed pressure leaching tests on converter matte obtained from the Lonmin Base Metals Refinery (BMR). Qualitative XRD analysis of the first stage leach residue obtained from the Lonmin BMR also yielded similar results.

Hofirek and Kerfoot (1992) as well as Hofirek and Nofal (1995) investigated the second stage high pressure sulphuric acid/oxygen leaching of first stage leaching residue at the Rustenburg BMR. The dominant mineralogical phases present in the feed material were the same as those mentioned above. According to the proposed

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

reaction mechanism, the rapid dissolution of copper from digenite by direct acid leaching shown by reaction (1) dominates the initial stages of the second stage leach:

$$Cu_9S_5 + 4H_2SO_4 + 2O_2 \rightarrow 5CuS + 4CuSO_4 + 4H_2O \qquad (1)$$
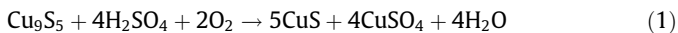
Leaching of covellite can proceed via direct oxidation or by acid leaching, as shown by reaction (2) and reaction (3), respectively.

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

$$CuS + H_2SO_4 + 0.5O_2 \rightarrow CuSO_4 + S + H_2O \qquad (3)$$
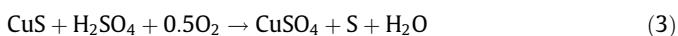
The millerite in the feed can either be converted to polydymite, as shown in reaction (4), or the nickel can be dissolved by direct oxidation (reaction (5)):

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

$$NiS + 2O_2 \rightarrow NiSO_4 \qquad (5)$$
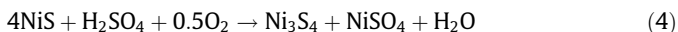
The overall reaction for the dissolution of polydymite that was proposed is given by reaction (6):

$$Ni_3S_4 + 7.5O_2 + H_2O \rightarrow 3NiSO_4 + H_2SO_4 \qquad (6)$$
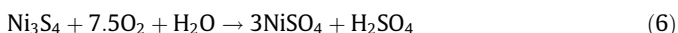
Grewal et al. (1992) studied the high pressure oxidative leaching of a copper refinery residue containing copper, predominantly as Cu_2S and $Cu_{1.96}S$, as well as precious metals. In correspondence with the copper leaching mechanism proposed by Rademan et al. (1999), it was determined that various intermediate copper sulphides such as $Cu_{1.76}S$ were formed during the copper dissolution. The further leaching of these compounds to form CuS was however much faster than the leaching of CuS itself. The proposed reaction pathway therefore considered the dissolution of Cu_2S and $Cu_{1.96}S$ to occur via two steps, with the formation of CuS as an intermediate product. In the presence of acid, the dissolution of Cu_2S in the first step followed a reaction similar to reaction (1). If excess acid was available the dissolution of CuS produced could occur simultaneously according to reaction (3).

Results published by Ruiz et al. (2007), who investigated the high pressure sulphuric acid/oxygen leaching of white metal, support the proposed reaction pathway whereby the leaching of chalcocite and other non-stoichiometric copper sulphides occurs in two stages with the formation of CuS as an intermediate product. Padilla et al. (2008) investigated the dissolution of sulphidised chalcopyrite in a high pressure sulphuric acid environment. Leaching of CuS was reported to occur by the same reactions discussed above (reactions (2) and (3)). This study also reported on the fact that the presence of ferric ions contributes to the leaching of metal sulphides. An indirect leaching mechanism was proposed for systems where ferric ions are present whereby metal sulphides are oxidised by Fe^{3+} where after the produced Fe^{2+} is re-oxidised by oxygen. The degree to which this influences the overall leaching rate has not been determined (Padilla et al., 2008).

Limited information is available about the PGM dissolution mechanism. Fugleberg et al. (1995) investigated the dissolution of rhodium during high pressure copper leaching to determine the most important operating parameters, but no information regarding reaction mechanisms and leaching kinetics were published. It is believed that the dissolution of PGMs proceeds according to reaction (7) (Steenekamp, 2009):

$$Me + 0.5O_2 + H_2SO_4 \rightarrow MeSO_4 + H_2O \qquad (7)$$
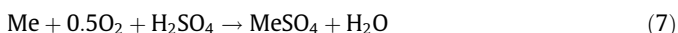
1.2. Effect of operating conditions

Ruiz et al. (2007) investigated the effect of stirring speed, temperature, sulphuric acid concentration, oxygen partial pressure, particle size distribution of the feed, and leaching time on the leaching of white metal. The temperature did influence the leaching kinetics. At temperature below 130 °C, the fast kinetics of the formation as CuS as an intermediate product was observed initially, followed by slower reaction kinetics as CuS dissolution proceeded. At higher temperatures, the two reaction steps were found to overlap and proceed at a faster rate, making it difficult to distinguish between the kinetics of the two steps.

The effect of oxygen pressure on the copper dissolution was investigated at temperatures of 130 °C and 150 °C. At the lower temperature, the oxygen partial pressure had a very small effect on the copper dissolution rate. At the higher temperature, however, increasing the oxygen partial pressure from 203 kPa to 608 kPa increased the copper dissolution rate, but further increasing the oxygen partial pressure did not have an influence on the copper dissolution. At high temperatures the leaching reactions proceed at a much faster rate, hence requiring a higher rate of oxygen addition for the reactions to occur. At the low oxygen partial pressure, the availability of oxygen and the transfer of oxygen to the reaction surfaces are limiting the rate at which the leaching reactions can proceed (Ruiz et al., 2007).

Maximum copper dissolution was achieved at an acid concentration of approximately 0.05 mol/l, whereafter dissolution decreased slightly with increasing acid concentration. This observation was ascribed to the fact that oxygen solubility decreases with increasing sulphuric acid concentration. At the conditions studied, it was observed that particle size did not have a significant effect on the rate of copper leaching. Slightly lower dissolution was achieved for the range of largest particle sizes, possibly because of diffusion effects within the particles becoming more significant (Ruiz et al., 2007).

Fugleberg et al. (1995) investigated the effects that acidity, oxygen pressure, and temperature have on the dissolution of rhodium during high pressure copper leaching. Temperature was identified as the parameter with the largest influence on rhodium dissolution, causing the dissolution to increase from 10% at 115 °C to 80–90% at 140 °C.

2. Experimental

2.1. Equipment

A 2 l Büchi Polyclave Type 3 pressure reactor manufactured from Hastelloy® was used for the experimental work. The autoclave is equipped with a Cyclone 300 magnetic stirrer drive, the speed of which was set manually at a constant rate. An anchor stirrer was used for all the tests. A pipe extending from a standard connector on the reactor cover plate into the reactor was used to sparge oxygen into the leaching solution, the flow rate of which was manipulated manually by adjusting a needle valve in the supply line. The reactor was equipped with a pressure gauge, and the pressure was controlled manually by adjusting the gas purge valve as well as the oxygen flow rate. The temperature of the vessel contents was controlled by a programmable controller utilising electric heating elements located around the reactor shell and a switch relay valve controlling the flow of cooling water through the reactor shell. Samples were taken from the reactor bottom drain valve. To prevent the sample leaving the reactor from flashing as a result of the sudden pressure drop, a hose with an additional valve was connected to the drain valve outlet. The sample was kept in the tube between the drain valve outlet and the additional valve until this sample had cooled down to a temperature below its boiling point.

2.2. Experimental design and operating conditions

Based on the literature study and practical considerations, three operating variables were identified as potential control variables