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Characterizing the leaching of sperrylite ($PtAs_2$) in cyanide-based solutions

James M. Mwase*, Jochen Petersen

Hydrometallurgy Laboratory, Department of Chemical Engineering, University of Cape Town, Rondebosch, South Africa

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ABSTRACT

The mineral sperrylite ($PtAs_2$), unlike other Pt minerals, has shown to be resistant to cyanide leaching, even at elevated temperatures of 50 °C. This has prevented further development of a two-stage heap leaching process, of which the second stage is cyanide leaching for a Platreef ore, due to a considerable portion of the Pt being present as sperrylite.

Through a comprehensive set of leaching tests, this study has shown that sperrylite leaches slowly in cyanide due to eventual passivation. The addition of ferricyanide to the cyanide solution results in significantly more Pt being leached (up to 16 times) than with cyanide only under identical process conditions. However, over time passivation occurred in this system also, but can be seemingly be overcome by filtering, rinsing and re-suspending the sperrylite. This was further investigated using a reactor system continuously fed with a ferricyanide-cyanide to leach a fixed bed of sperrylite mineral. Again, gradual passivation of the mineral phase was observed, which was fully reversible following a day of feeding with distilled water.

XPS analysis of fresh and leached mineral indicated a depletion of As on the mineral surface, which tallied with an observed preferential leaching of As during leaching, at least initially. As a result, it is postulated that a less cyanide-soluble compound of the form $PtAs_{(X)}$ forms, where x is $<$ 2. The ease with which the leaching process can be restarted after rinsing the mineral indicates that the adsorption of solution species is the key step in forming a passivating layer. This adsorption is potentially favoured by the gradual surface transformation.

Finally, an electrochemical study confirmed that the ferricyanide-cyanide system facilitated an electron transfer reaction at the sperrylite surface with the likely oxidation of As and reduction of the ferricyanide. Gradual passivation of the surface was also observed in this system.

1. Introduction

A two-stage heap leaching process was developed as an alternative to the conventional concentrate-smelt-refine process to treat Platreef ore (Mwase et al., 2014; Mwase et al., 2012; Eksteen et al., 2012). The process consists of a thermophile heap bioleaching stage which removes large portions of Cu, Ni and Co from the ore for separate recovery and nearly completely oxidises all sulphide present. This is followed by a cyanide leach stage at 50 °C which intends to mobilise Au, Pd and Pt. The process was tested at laboratory scale using columns to simulate heap conditions (Mwase et al., 2014; Mwase et al., 2012). While the bioleaching stage achieved the desired performance, the cyanide leaching rapidly mobilised Pd quantitatively and 90% of Au, but only 60% of the Pt was extracted over a 60 day period. The unleached portion of Pt was almost entirely attributed to sperrylite ($PtAs_2$) in Platreef materials as the main Pt bearing mineral in this ore. Sperrylite constitutes 21% of all the platinum group minerals in Platreef ore. The total platinum group mineral concentration is 3 g/t. Other Pt species (mainly tellurides) leached readily in cyanide.

Sperrylite is a chemically stable compound that does not readily decompose or alter through normal weathering processes such as those that affect base metal minerals like chalcopyrite. There is no information in literature that outright states the oxidation states of Pt or As in sperrylite. The most common valence states of As are -3, 0, $+3$ and $+5$ (Marinov and Brebbia, 2010; Henke and Hutchison, 2009). However, As in arsenic-rich (arsenian) pyrite and many arsenide and arsenosulpide minerals has been found to have a net valence of -1 (Marinov and Brebbia, 2010; Henke and Hutchison, 2009; Jones and Nesbitt, 2002; Nesbitt and Reinke, 1999). This is because the As is present in multiple/mixed oxidation states in these minerals. A net oxidation state of -1 for As would mean that in sperrylite Pt is in the common and most likely state of $+2$ (Seymour and O'Farrelly, 2001; Giandomenico, 2000). Solid state nuclear magnetic resonance (NMR) analysis was conducted on a micronized sample of sperrylite by the NMR and CD Unit at Stellenbosch University, South Africa. The results, although inconclusive, strongly suggested that the oxidation state of Pt

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* Corresponding author.
E-mail address: j.mwase@ulg.ac.be (J.M. Mwase).

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was most likely a lower state, of which +2 is the most probable (Mwase, 2016). At negative valencies arsenic (in a compound) is reported to be least soluble (Andserson, 2010; Vladimir and Moran, 2006). Hence it is suggested that successful leaching of sperrylite requires the oxidation of As (or the part of the As that are at negative valencies) to a higher, more soluble oxidation state (either +3 or +5), thus breaking the chemical bond with Pt and releasing it into solution.

A study conducted on Platreef concentrate by Mwase et al. (2012) suggests that the reaction between sperrylite and cyanide is not influenced significantly by temperature or reagent concentration, but is most likely a diffusion controlled reaction. It was postulated that some form of passivation may occur at the surface of the mineral in that a small quantity of Pt leaching into solution leaves behind an As layer which passivates the surface of the mineral. This means that there is partial oxidation of the As from a lower state to elemental or a transitional state. This would imply that if more oxygen, or any such suitable oxidant, was available in solution, then the As could be fully oxidised, allowing a higher rate of Pt extraction. However, Mwase (2016) showed through leaching test work, that even pure oxygen has virtually no influence on the cyanide leaching of sperrylite, possibly due to its low solubility in solution. Ferricyanide has been investigated as an alternative oxidant to oxygen in the cyanide leaching of certain gold and silver sulphides which are similarly slow-leaching in cyanide (Xie and Dreisinger, 2009; Xie et al., 2008). It was found to slightly improve the leaching of gold from these minerals.

The reduction potential for ferricyanide is slightly lower than oxygen in alkaline aqueous solutions ($pH > 7$) at 25 °C (Greenwood and Earnshaw, 1997; Xie and Dreisinger, 2007; Song and Zhang, n.d.), as seen in the equations below.

$$Fe(CN)_6{}^{3-} + e \rightarrow Fe(CN)_6{}^{4-}\ E^\circ = 0.36\ V\ (SHE) \tag{1.1}$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-\ E^\circ = 0.4\ V\ (SHE) \tag{1.2}$$

However, the oxidation capability of ferricyanide can be maintained at a relatively high level due to its high solubility in cyanide solution. Ferricyanide and ferrocyanide are stable over a wide pH range and will not react with cyanide (Xie and Dreisinger, 2007). Reagents of the peroxygen (hydrogen peroxide and calcium peroxide) and per-manganate (potassium permanganate) species have all been studied as potential alternative oxidants to oxygen in cyanide leaching of gold and silver (Xie and Dreisinger, 2009; Xie et al., 2008). However, none of these have been successfully applied in practice due to high cost and their tendency to react preferentially with free cyanide at the high concentrations required to make them effective. The study by Mwase (2016) also showed that increasing the amount of cyanide concentration in the cyanide-only system had no influence on the amount of Pt leached.

This study, through leaching tests, surface analysis and electrochemical techniques, investigates and attempts to explain the slow leaching of sperrylite in cyanide solution. Furthermore, ferricyanide has been evaluated to determine if it can improve the Pt extractions by acting as an oxidant. From this investigation it can be determined if ferricyanide leaching is a viable option to explore for cyanide-based heap leaching of Pt from Platreef ore. Having postulated that the slow leaching of sperrylite in cyanide is due to the occurrence of a change at the surface of the mineral during leaching, X-ray photo-electron spectroscopy (XPS) analysis of leached samples has been identified as the most suitable method of investigation as demonstrated in other studies (Sasaki et al., 2010; Parker et al., 2003; Klauber et al., 2001; Yuzer et al., 2000; Hackl et al., 1995; Mycroft et al., 1995; Pratt et al., 1994). There are some studies (Arena et al., 2016; Olvera et al., 2015; Yang et al., 2013; Khoshkhoo et al., 2014; Hackl et al., 1995) that have used electrochemistry and XPS to explain specifically the phenomenon of passivation in chalcopyrite leaching, although it is acknowledged that chalcopyrite passivation it is not a similar system to the one explored in this study.

Table 1
Weight percentages of Pt and As in sample compared with literature values.

	Sample		Literature	
	Pt	As	Pt	As
Weight %	56.1	43.9	56.6	43.4

2. Materials

A sample of high purity sperrylite mineral was obtained from the Wallbridge Mining Company of Canada, courtesy of Lonmin Plc. The sample originated from the nickel ore deposit of the Sudbury Basin in Ontario Canada. Originally, the sample was in what appeared to be crystalline form of various sizes from 2 mm down to fines in the micron range. For the leaching experiments sub-samples of 3.5 g (capacity of the micronizer) were micronized to minus 5 μm. Analysis on a micronized sample using XRD (X-ray powder diffraction) showed the samples was 100% sperrylite. This was confirmed using scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDS) on the same sample, which indicated some expected trace impurities of Cu, S and Si. However the weight and atomic percentages of Pt and As (Table 1) were similar to what was reported in the literature (http://rruff.info/doclib/hom/sperrylite.pdf).

3. Methods

3.1. Leaching tests

The tests were conducted in a batch stirred tank reactor (BSTR) configuration, using a 500 mL jacketed glass reactor agitated with a magnetic stirrer. In this first set of leaching experiments, a 1 g sample of sperrylite was leached in 500 mL of a 5 g/L NaCN solution. The pH of the solution was kept in the range of 10.5–10.9 using bicarbonate buffers. Temperature was maintained at 50 °C for 5 days using a water bath. After the run, the solution was vacuum filtered and the residual solids re-suspended in fresh solution and leached again for 5 days. Before re-leaching the solids, a small sub-sample was set aside for SEM-EDS and XPS analysis. This was repeated for a 3rd run. This experiment was repeated in its entirety for a second time. In similar fashion, a set of three 5-day runs were conducted with 1 g/L of sperrylite in 500 mL of a 5 g/L NaCN, 5 g/L $K_3[Fe(CN)_6]$ solution. The pH was kept in the range of 10.5–12 using bicarbonate buffers. Again, this was repeated in its entirety. No sparging of air into solution was done, but because the vessel was not air-tight, some atmospheric air would enter the reactor and solution. As indicated in the introduction, Mwase (2016) found that the presence of even pure oxygen had no effect on the leaching of sperrylite in cyanide solutions. The temperature was monitored with a thermometer. Samples of solution were withdrawn using a syringe at various intervals during each run and vacuum filtered. Samples were analysed via inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the amount of Pt and As in solution. Additionally, the pH of the samples was measured using a standard pH meter.

The cyanide solution was prepared from pure sodium cyanide supplied by Merck South Africa, and a combination of 1.01 g/L of sodium bicarbonate and 9.32 g/L sodium carbonate was used to keep the pH above 9.6. Ferricyanide was added as analytical-grade potassium ferricyanide purchased from Sigma-Aldrich South Africa.

3.2. Continuously fed tube reactor

A 500 mg bed of micronized sperrylite sample was fixed in between 2 beds of fine quartz in a thin glass tube with a diameter of 5 mm and length of 20 cm (Fig. 1). The quartz material was washed in dilute HCl (15%) and dried prior to use. Glass wool was placed at the ends of each