Characterizing the leaching of sperrylite (PtAs₂) in cyanide-based solutions

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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 less than 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.

Keywords: Sperrylite, cyanide, leaching, electrochemistry, XPS, Platreef ore
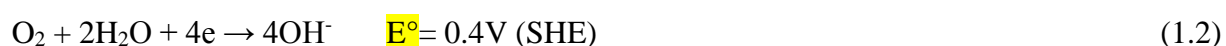
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1.0. Introduction

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 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 (Anderson, 2010; Vladmir 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 oxidized, 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.

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

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

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 per-oxygen (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., 2015; 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.

2.0. 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).

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

3.0. 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 5g/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 1g/L of sperrylite in 500 mL of a 5g/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 (Figure 1). The quartz material was washed in dilute HCl (15 %) and dried prior to use. Glass wool was placed at the ends of each tube to act as a filter, preventing loss of particles at the entrance and exit. The tube was

held horizontally in a water bath using a clamp and retort stand to run the experiment at 50°C (Figure 1). A section of the silicon tubing was coiled prior to entry in the mini-column to act as a heat exchanger and allow heating of the solution before contacting with the sperrylite. This set-up was placed inside a fume hood for safety. A combination of 5 g/L sodium cyanide and 5 g/L potassium ferricyanide solution, buffered with 1.01 g/L of sodium bicarbonate and 9.32 g/L sodium carbonate, was fed through the tube at a rate of 2 L per day using a peristaltic pump. Initially solution was fed to the column until it reached the entrance and then the flow was stopped before it made contact with the sperrylite. Then the column was completely immersed in water and the bath heated to 50°C. After about 20 minutes, giving the system time to reach 50°C, the flow of solution was resumed and the effluent collected in clean 5 L plastic containers. Samples were collected after 1, 4 and 8 hours and thereafter every 24 hours for analysis of Pt and As using ICP-OES.
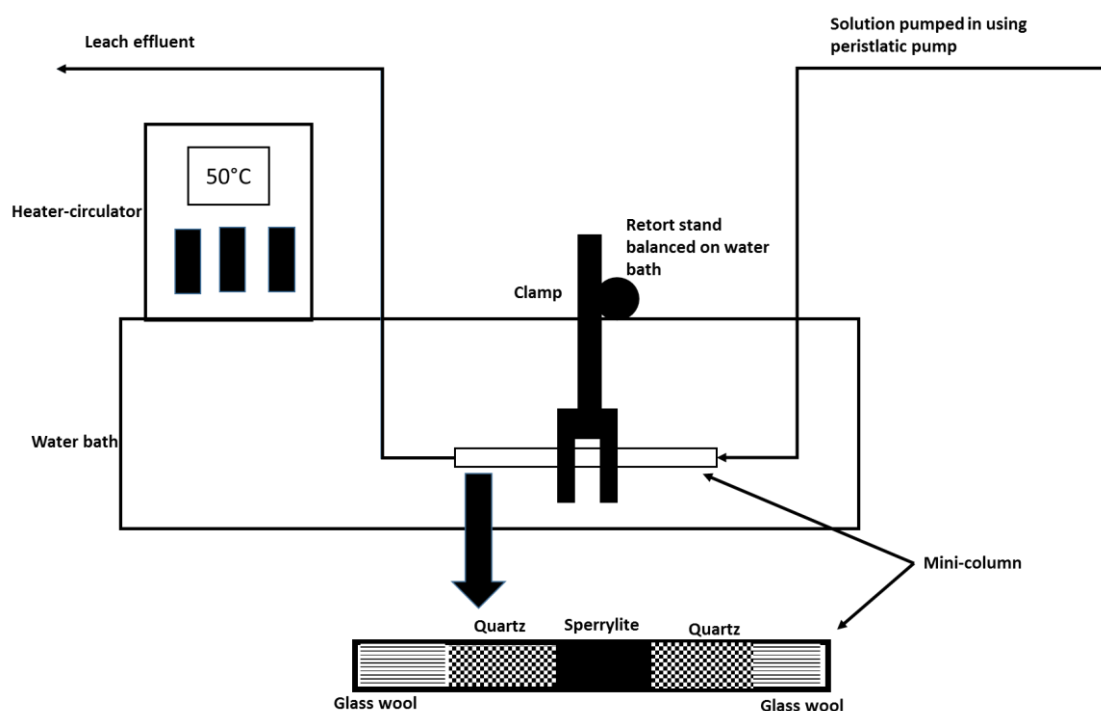

Figure 1: Schematic drawing for mini-column and experimental set-up for continuously fed leaching experiment

3.3. X-ray Photoelectron Spectroscopy (XPS) analysis

The XPS equipment used was the PHI 5000 Scanning ESCA Microprobe located at the Department of Physics at the University of the Free State, Bloemfontein, South Africa.

A 100 μm diameter monochromatic Al Kα x-ray beam (hν = 1486.6 eV) generated by a 25 W, 15 kV electron beam was used to analyse the different binding energy peaks. The pass energy was set to 11 eV, giving an analyser resolution ≤ 0.5 eV. Multipack version 9 software was utilized to analyse the spectra to identify the chemical compounds and their electronic states using Gaussian–Lorentz fits. A low energy Ar^+ ion gun and low energy neutralizer electron gun were used to minimize charging on the surface.

Samples of sperrylite, untreated and after specific leach tests were mounted onto a small holder cup of area 3 mm^2. The initial analysis was conducted on the surface of the sample to identify elements present and quantities prior to depth profiling. The depth profiling involved an identical analysis for two minutes, resulting in a more penetrative scan (36 nm from the surface).

3.4 Electrochemical Study

The equipment used in these experiments consisted of a glass reactor to hold the solution (cyanide and ferricyanide-cyanide) and a standard three-electrode set-up. The working electrode was a mineral electrode constructed from a large sperrylite crystal embedded in an epoxy resin block with one face of the crystal exposed. Using a high resolution image from a microscope, the surface area of the exposed face of the crystal was calculated to be 1.3 x 10^{-6} m^2. This block was permanently connected to a brass rod with the other end threaded to screw into an overhead stirrer. The other two electrodes were a reference electrode (saturated calomel electrode-SCE) and counter electrode (platinum wire). All three electrodes were dipped into the solution in the reactor vessel (Figure 2).

The mineral electrode was attached to an over-head stirrer to rotate the electrode for controlled mass transfer effects and agitation. The electrode was rotated at a speed of 1600 rpm. The electrodes were connected to a Gamry™ potentiostat with software, imbedded in a regular desktop computer. The reactor was jacketed and ran at a maximum temperature of 40°C (beyond that temperature the epoxy coating holding the crystal would crack) using a water bath. For safety the entire rig was placed in a bench top fume hood to create a physical barrier between other laboratory users and the cyanide experiment. The experiments involved taking measurements and observing trends through open circuit potential, cyclic voltammetry and

chronoamperometry. Before commencing a set of experiments the mineral electrode was polished on Bauxite (0.3 µm) on a Streuers' polish cloth.
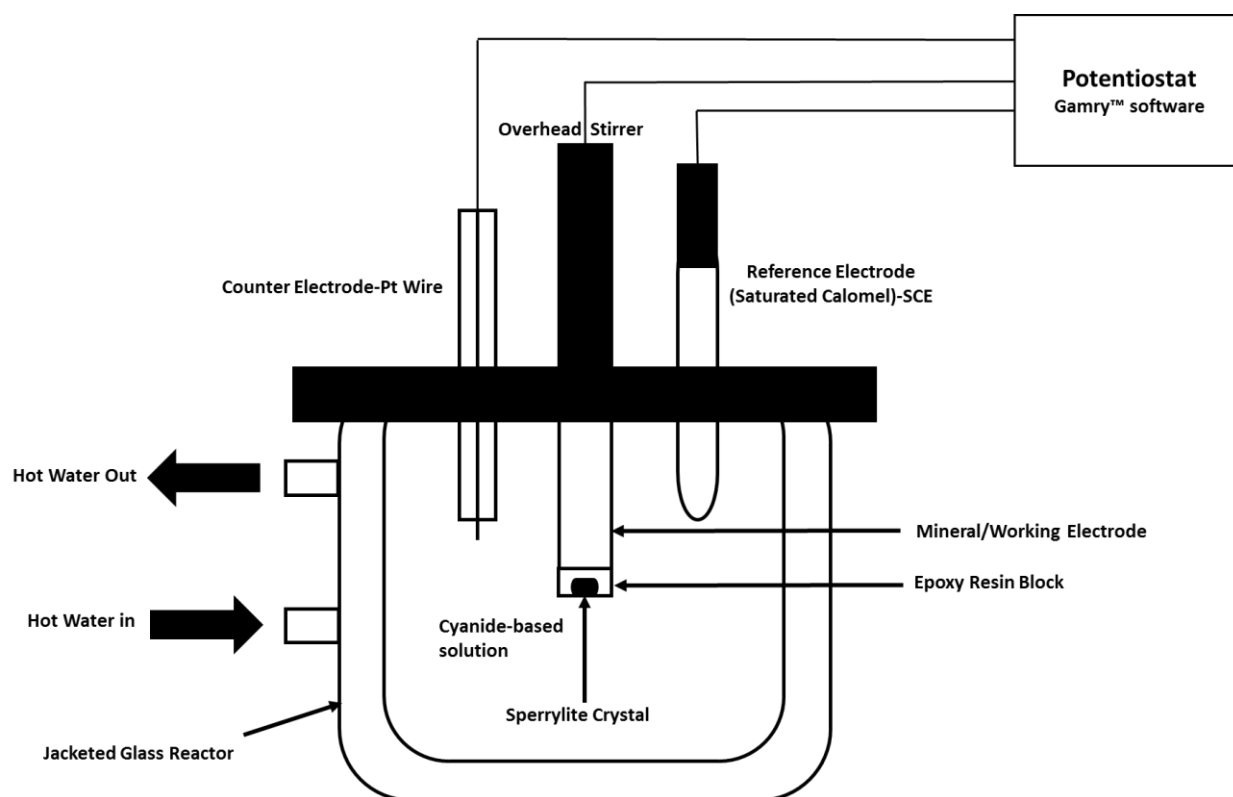

Figure 2: Schematic drawing of experimental set-up for electrochemical study

4.0. Results and Discussion

4.1. Leaching Tests

Curves for all the experiments are plotted as concentration in solution (mg/L) versus time. The percentage extractions were very low, in the range ≤6 % for the cyanide-only system and ≤15% for the ferricyanide-cyanide system. A comparison between the amounts extracted in the two systems, cyanide-only (Figures 3 and 4) and ferricyanide-cyanide (Figures 5 and 6) proves the hypothesis that the use of a suitable oxidant results in improved leaching of the sperrylite. The Pt levels extracted in the ferricyanide-cyanide systems are in the order of 12-16 times more than what is extracted by the cyanide-only systems. Further, Mwase (2016) showed that on its own, ferricyanide was ineffective in leaching sperrylite. This demonstrates that it acts as an oxidant, with cyanide acting as the complexing agent for the dissolved Pt.

Looking at the cyanide-only system, Figure 3 and Figure 4 show that in all runs there is a sudden increase in leaching in the course of the second day and a stagnation or decline in concentration after the 4th day. Over the first day, the first runs show appreciable leaching, whereas the second runs show only marginal and the third runs essentially no initial leaching. Otherwise patterns are less clear. The final extent of leaching between 1st, 2nd and 3rd runs varies and the leach trends between Pt and As are not always consistent. It can be seen, however, that even with fresh solution, a certain amount of Pt dissolved is not exceeded. It can be argued that with subsequent runs never is more Pt leached than in the first run and therefore the dissolution of Pt might reach a solubility constraint.
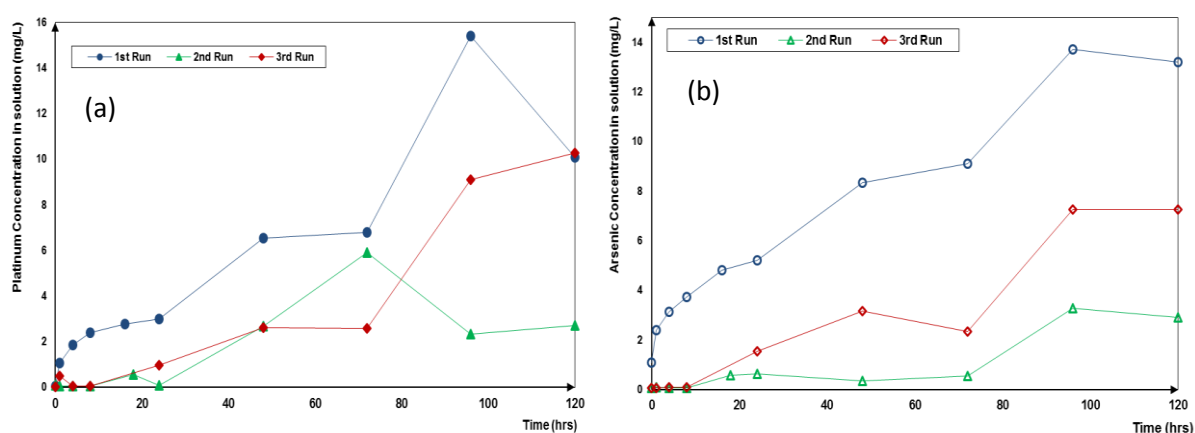

Figure 3: Pt(a) and As(b) leach curves for cyanide-only leaching experiments using 5 g/L NaCN, 500 mL of solution at 50°C and 1 g micronized sperrylite in the 1st run and the residual sperrylite from each completed run used in the following.
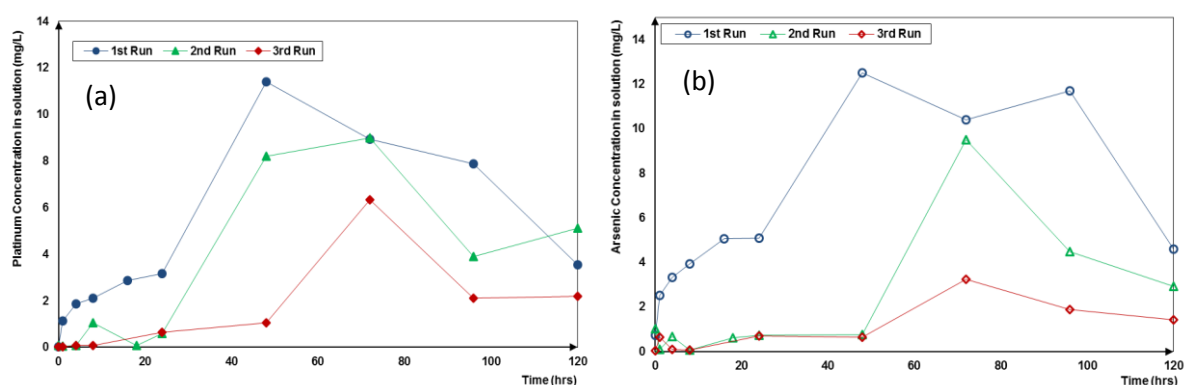

Figure 4: Pt(a) and As(b) leach curves for repeated cyanide-only leaching experiments using 5 g/L NaCN, 500 mL of solution at 50°C and 1 g micronized sperrylite in the 1st run and the residual sperrylite from each completed run used in the following.

For the ferricyanide-cyanide system (Figure 5 and Figure 6), almost identical leaching patterns are observed in the repeat reactors, and the leach curves increase steadily over the first 3 days

of the run, slowing or levelling thereafter. The first run levels off more rapidly and at lower concentrations than subsequent runs. This rules out a solubility constraint in this system but rather indicating a more complex interaction at the surface of the mineral particles. It appears that the use of the ferricyanide has a significant effect on changing the surface structure of the mineral particles over a period of time.
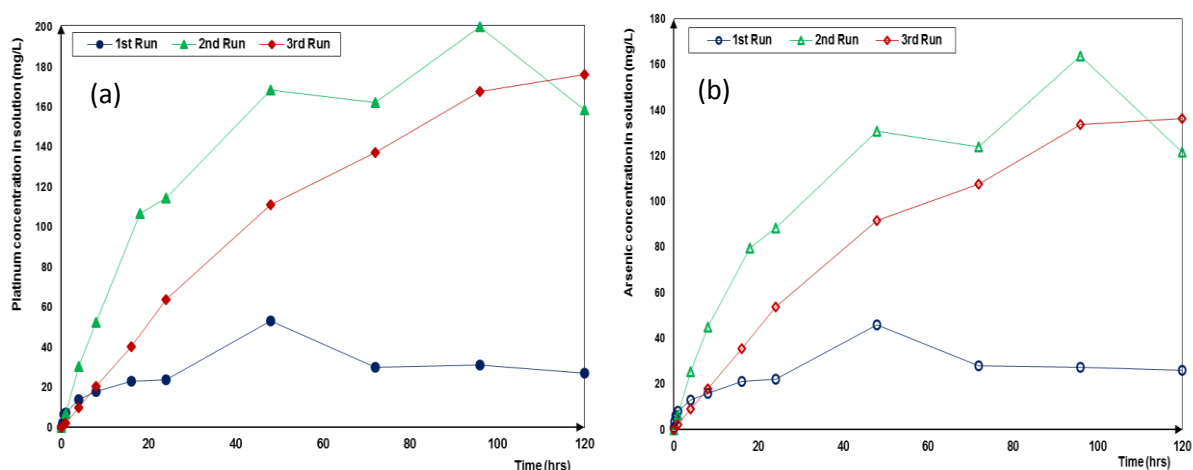

Figure 5: Pt(a) and As(b) leach curves for cyanide-ferricyanide leaching experiments using 5 g/L NaCN, 5 g/L K$_3$[Fe(CN)$_6$] in 500 mL of solution at 50°C and 1 g micronized sperrylite in the 1st run and the residual sperrylite from each completed run used in the following.
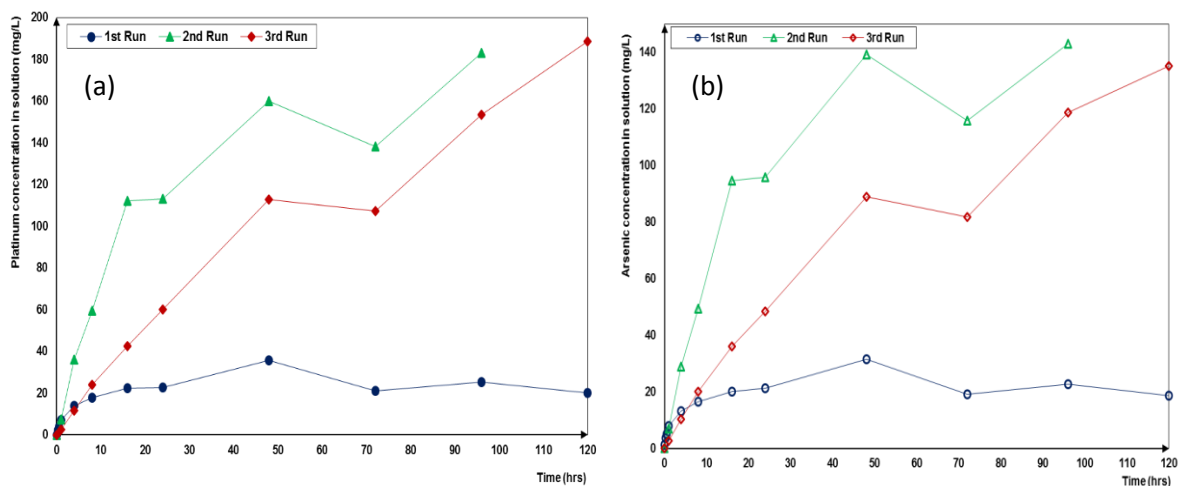

Figure 6: Pt(a) and As(b) leach curves for repeated cyanide-ferricyanide leaching experiments using 5 g/L NaCN, 5 g/L K$_3$[Fe(CN)$_6$] in 500 mL of solution at 50°C and 1 g micronized sperrylite in the 1st run and the residual sperrylite from each completed run used in the following.

The curves for arsenic (Figures 3(b) to 6(b)) are nearly identical to those of the Pt in each system, and the quantities were similar, showing that leaching occurs by dissolution of both components. The molar ratios of Pt to As in solution were analysed for both the cyanide-only system (Table 2) and the ferricyanide-cyanide system (Table 3). The points correspond with

the leaching points from the Pt and As leach curves. The values in Table 2 indicate that in all runs As leaches preferentially over Pt, at least initially, resulting in the Pt:As ratio to be well below the target value of 0.5. Only towards the end of the runs, after 5 days, is this ratio met in some cases and exceeded in others, indicating the As may in fact precipitate out of solution again.

Table 3 shows the molar ratios of Pt to As in solution for the ferricyanide-cyanide experiments. In the case of the first run for each experiment it stays at 0.5 after levelling off, consistent with no more leaching occurring, and with the 2nd and 3rd runs it is still at 0.5, showing not only continuous leaching but consistent leaching of the sperrylite mineral as compared to the preferential leaching of As in the cyanide-only experiments.

Table 2: Molar ratio of Pt to As in solution for repeated leaching experiments for cyanide-only system (values in parenthesis are seen as outliers)

	1st Exp.			Repeat		
Time (hrs)	1st Run	2nd Run	3rd Run	1st Run	2nd Run	3rd Run
1	0.2	0.2	(2.8)	0.2	0.2	0.0
4	0.2	0.3	0.2	0.2	(0.0)	0.3
8	0.2	0.4	0.2	0.2	(5.8)	0.5
16	0.2	0.4		0.2	0.1	
24	0.2	0.1	0.2	0.2	0.3	0.4
48	0.3	(3.0)	0.3	0.4	(4.1)	0.6
72	0.3	(4.3)	0.4	0.3	0.4	0.8
96	0.4	0.3	0.5	0.3	0.3	0.4
120	0.3	0.4	0.5	0.3	0.7	0.6

Table 3: Molar ratio of Pt to As in solution for repeated leaching experiments for cyanide-ferricyanide system

	1st Exp.			repeat		
Time (hrs)	1st Run	2nd Run	3rd Run	1st Run	2nd Run	3rd Run
1	0.3	0.4	0.4	0.2	0.4	0.4
4	0.4	0.5	0.4	0.3	0.5	0.4
8	0.4	0.5	0.4	0.3	0.5	0.5
16	0.4	0.5	0.4	0.4	0.5	0.5
24	0.4	0.5	0.5	0.4	0.5	0.5
48	0.5	0.5	0.5	0.4	0.5	0.5
72	0.4	0.5	0.5	0.4	0.5	0.5
96	0.4	0.5	0.5	0.4	0.5	0.5
120	0.4	0.5	0.5	0.4		0.5

The batch leach tests thus indicate that the cyanide leaching of sperrylite in the presence of ferricyanide follows a different reaction mechanism compared to the leaching in its absence. The cyanide-only system shows two reaction stages, with the first proceeding over the first day of leaching and becoming increasingly less significant with each repeat run. Significantly more As is leached during this phase than Pt, therefore this phase could relate to the dissolution of surface-oxidised As compounds. A secondary leach phase, which releases significantly more Pt, commences only after this initial day. In all cases leaching levels off or declines after 3-4 days, indicating a surface inhibition, or solubility constraint.

The batch leaching results in the ferricyanide-cyanide system do not indicate the same two-stage mechanism; or, given the much higher initial rates, it is not discernible from the measured data. Although similarly to the cyanide-only tests the leach curves level off after 3-4 days, the fact that this happens at a different level in each run (and at much higher levels than in the cyanide-only experiments) rules out a solubility constraint. It, however, supports the formation of an inhibiting surface layer or deposit, which is removed during the filtration/washing/drying stage between runs.

4.2 Continuously fed reactor

It was initially assumed that the dissolution in the batch tests was either limited by a solubility constraint or by reagent supply, leading to the levelling off after each run. Either way, renewed leaching resulted after replacing the leach solution. Based on this assumption, it was decided to test the continuous leaching of a sperrylite sample in the same combined ferricyanide-cyanide solution as used in the batch tests, but continuously supplying fresh leach solution.

Figure 7 shows the Pt and As leach curves plotted as cumulative amounts in mg extracted versus time. This form of representing the data was chosen over percentage extraction because the percentage extraction was low, amounting to 7-8% extraction for each element over the entire experiment. Similar to the results from the ferricyanide-cyanide batch leaching experiments, the rates of Pt and As leaching appear similar and follow an almost identical pattern, with the Pt:As molar ratio close to 0.5 at all times. Unexpectedly, however, the leaching pattern over time is also similar to the leach curves observed in the batch experiments in that the leaching rate declines after some time. This is observed in Figure 7 after day 8. A decision was taken, therefore, to subject the sperrylite particles in the bed to a short water wash (similar to what the particles would have experienced during filtration and rinsing between runs in the batch experiments). Since the tube could not be emptied to recover and replace the sperrylite, distilled water was instead pumped through the bed for 24 hours at a rate of 2 L/day. This was done on the morning of day 18. Then leaching with the ferricyanide-cyanide solution resumed on the morning of day 19, with the first sample point being at day 20 but this was taken as the 19th day of leaching hence the plot of the graph picks up from the point.

The effect of the wash with distilled water can be seen almost immediately. From 19th day of leaching the jump in the rate and extent of extraction is significant, compared to what it was from day 8 to day 18. This does add some credibility to the theory that passivation in the ferricyanide-cyanide system occurs due to the formation of unknown reaction products which deposit on the surface initially and not due to a change in the surface structure. These products hinder further leaching but can be washed off or re-dissolved to allow for continued and improved leaching. As can be seen in Figure 7 after day 30, the passivation starts to occur again, indicating that the formation of the inhibiting surface products must be linked to reaction products. In this context it is interesting to note that the onset of this passivation or inhibition coincides with the preferential leaching of As over Pt. Also, given there was no mechanical

disturbance of the bed when switching from leaching to water wash and back to leaching, the removal of the inhibiting substance is likely to follow a desorption mechanism and less likely to be any form of solid layer.
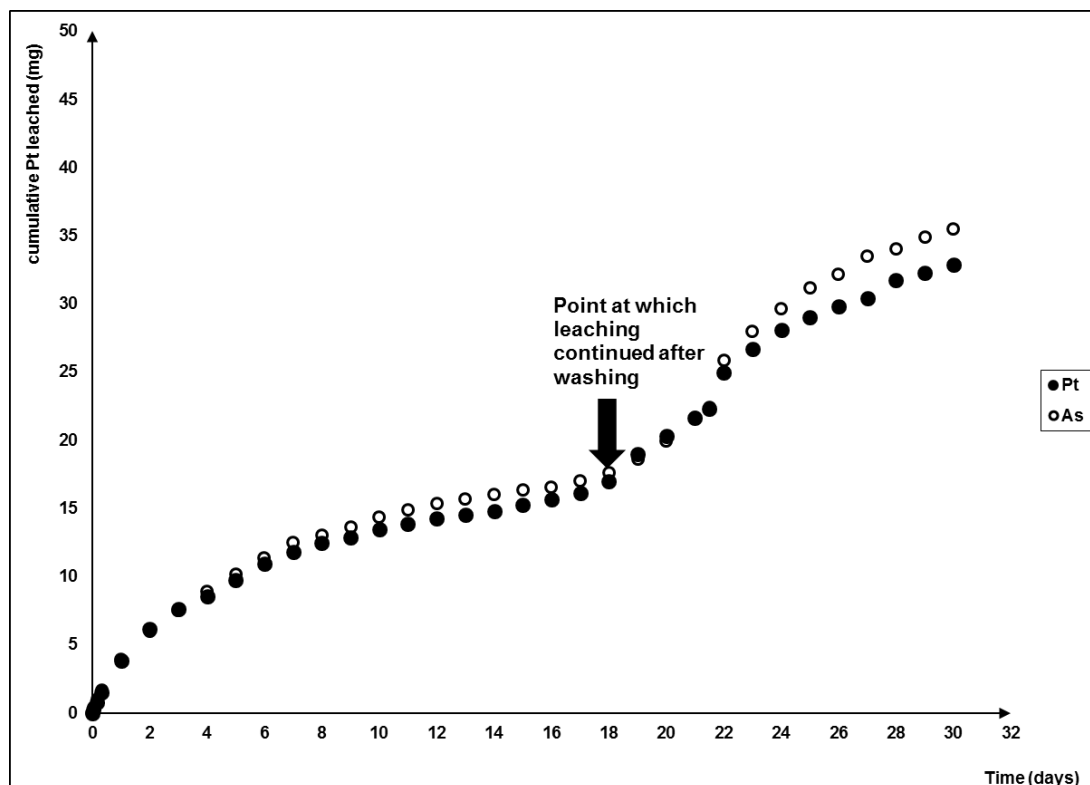

Figure 7: Pt and As leaching curves. 5 g/L NaCN, 5 g/L K₃[Fe(CN)₆], 500 mg sperrylite, 50°C, feed rate-2 L/day, pH 10.3-10.6

4.3 Surface Analysis

The leach test work has clearly identified the formation of surface layers or surface deposits that inhibit the progress of leaching. To further understand the mechanisms at play, various sperrylite samples were analysed using surface analysis techniques (EDS and XPS) as follows:

Sample 1: sample of the micronized sperrylite untreated;

Sample 2: taken after the third run in first set of the cyanide-only experiment (Figure 3);

Sample 3: taken after the first run of the first set of the ferricyanide-cyanide experiment (Figure 5);

Sample 4: taken after the third run of the first set of the ferricyanide-cyanide experiments (Figure 5).

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EDS analysis of the different samples was attempted to see whether a difference in As:Pt atomic ratio between the different samples could be detected, more specifically that Sample 1 would have a ratio consistent with literature (Sperrylite, n.d.), approximately 2:1, whereas in Sample 2 it should have one lower than 2:1 with the surface layers perhaps having less arsenic than Sample 1 (since proportionally more leached during the experiment), while Samples 3 and 4 would most likely remain at a ratio of 2:1 since the Pt:As ratio in solution for these systems was consistently around 1:2 (Table 3). The EDS analysis (Table 4) for all samples showed that the As:Pt atomic ratio, approximately at 2:1, and the weight percentages more less stayed the same, with at best a marginal shift to an enrichment in As. As this shows no significant change in the As:Pt ratio in the bulk of the sample, the focus turned to the XPS analysis to determine if any changes could be detected at the surface and near-surface of the samples.

Table 4: EDS analysis results for samples 1-4 from leaching tests

Sample	Weight %		Atomic %	
	Pt	As	Pt	As
Sample 1 (untreated-fresh)	56.9	43.1	33.7	66.3
Sample 2 (cyanide-only)	55.8	44.2	32.6	67.4
Sample 3 (cyanide-ferricyanide-1st run)	55.6	44.4	32.5	67.5
Sample 4 (cyanide-ferricyanide-3rd run)	55.7	44.3	32.6	67.4

Table 5: Atomic ratios of As:Pt in untreated sample of sperrylite, and treated in cyanide-only and cyanide-ferricyanide solutions

Sample	surface	36 nm depth scan
Sample 1 (untreated-fresh)	2.2 : 1	1.32 : 1
Sample 2 (cyanide-only)	2 : 1	1.62 : 1
Sample 3 (cyanide-ferricyanide-1st run)	1.82 : 1	1.89 : 1
Sample 4 (cyanide-ferricyanide-3rd run)	1.75 : 1	0.89 : 1

Table 5 shows some results from the surface scan and depth profiling of the different samples. As a start it is interesting to note that the untreated Sample 1 shows an enrichment of As on the surface but a depletion in the sub-surface. This could potentially point to the reason why especially in the cyanide-only experiments substantially more As than Pt is leached out in that,

potentially, the As has become surface-oxidised and thus water-soluble during the micronizing process. This is also supported by the fact that almost no As is leached initially during runs 2 and 3. The As depletion in the subsurface observed in the initial sample could be related to the As enrichment on the surface, having essentially diffused to the surface where it became oxidised.

The analysis of sample 2 indicates the correct balance between As and Pt on the surface and slight As depletion in the subsurface. During the cyanide-only leaching experiment in run 1 (Table 2) As was preferentially leached initially, but Pt leached preferentially after day 1, resulting it to 'catch up' with the As towards the end of the run. The subsurface remains As depleted, but not to the same degree as the unleached sample.

Samples 3 and 4 show a slight surface depletion of As, which may be consistent with the slightly preferential leaching of As over Pt (Pt:As ratios in solution of around 0.4-0.5, i.e. slightly in favour of As) during most of the ferricyanide-cyanide experiment (Table 3). As depletion from the sub-surface, however, is substantial, and appears to increase with the extent to which the sample has been leached. This could provide an important pointer towards what inhibits the leaching as time progresses: It is plausible that during leaching, As goes into solution preferentially, especially if it can be oxidised at the surface, leaving behind an As-depleted surface layer through which As needs to diffuse from the bulk mineral. The Pt follows into solution more gradually upon complexation with cyanide. As the thickness of the surface layer grows, the supply of As from the bulk becomes increasingly inhibited and thus the overall rate of leaching slows.

The $Pt4f_7$ peaks and binding energies in all 4 samples (Figure 8) from the XPS analysis are identical to those in Moulder et al. (1995) (Handbook of X-ray Photoelectron Spectroscopy), and the study by Avril et al. (2015) show that the Pt in all 4 samples was Pt^{2+}. The peak for the depth profile for the 36 nm scan shifts to the right (lower binding energies) quite noticeably in all samples. All compounds with Pt^{2+} in Moulder et al. (1995) have the $4f_7$ peak between 72 and 75 eV, while metallic Pt has a binding energy close to 71 eV and Pt^{4+} has a binding energy of above 75 eV. The shift of the $Pt4f_7$ peaks closer to 71 eV perhaps suggests a shift in the oxidation state of part of the Pt – a change to metallic Pt would have made leaching difficult in Samples 3 and 4.
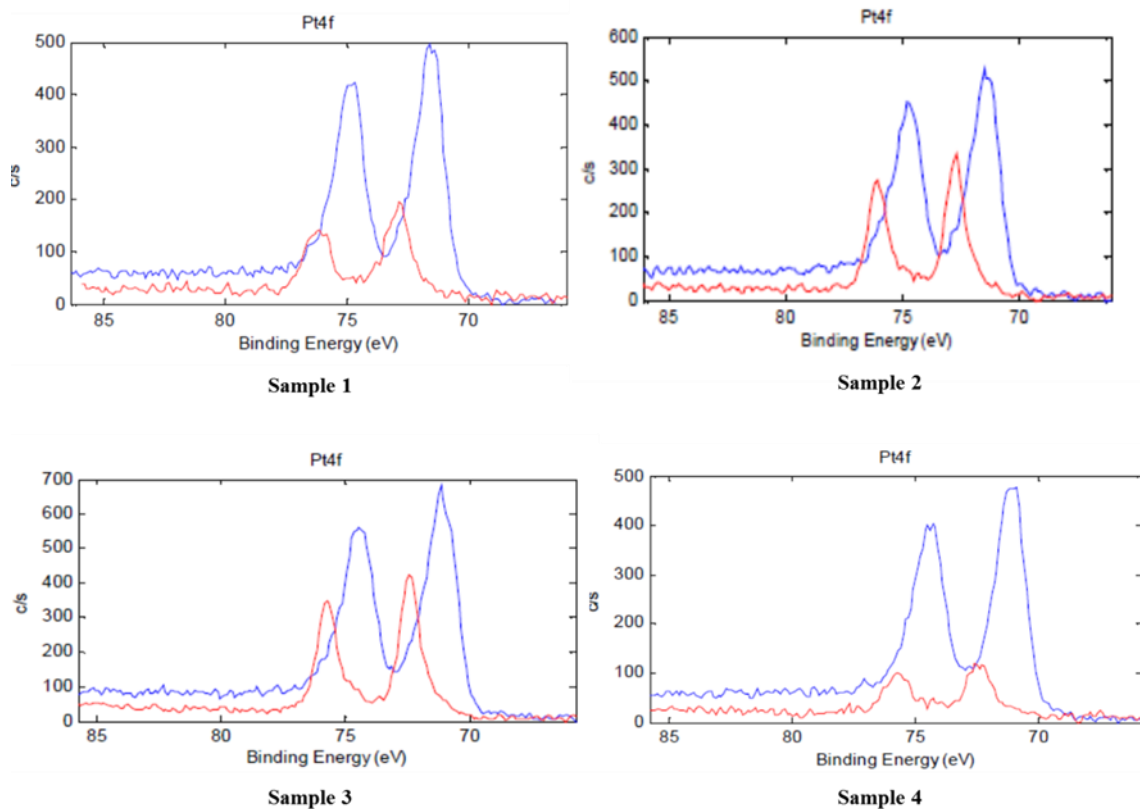
Figure 8: Pt4f XPS peaks for all 4 samples. Bottom curve represents survey at the surface of sample and top curve survey after 2 minutes of depth profile-penetration of 36 nm

For the most part the As3d peaks (and corresponding binding energies) for all 4 samples (Figure 9) did not match those in Moulder et al. (1995) or any other studies on arsenides and arsenic compounds. Coincidentally, all the data in the literature relates to As in the +5, +3 and 0 states and none were reported for the lowers oxidation states. A comparison with studies conducted by Nesbitt and Reinke (1999) on NiAs, and Jones and Nesbitt (2002) on $FeAs_2$ using XPS showed that although their peaks differ from those in Figure 9, they did find binding energies between 41-42 eV which is identical to the 41-42 eV range for the As3d peaks in this study, specifically for Samples 1, 3 and 4. Arsenic in NiAs and $FeAs_2$ is in the -1 oxidation state (Jones and Nesbitt, 2002; Nesbitt and Reinke, 1999) and hence, with those similar binding energies, it may also be in the -1 state in $PtAs_2$. As stated by Henke and Hutchison (2009), this oxidation state represents mixed or multiple oxidation states of As, not necessarily of an actual As(-I) species.

From Figure 9 the position of the peaks below a binding energy of 40eV for Sample 2, as compared to the other samples, is quite noticeable. Regardless of the oxidation state, As is not

known to have a binding energy of less than 40eV for its 3d peak based on currently documented compounds (Moulder et al., 1995).
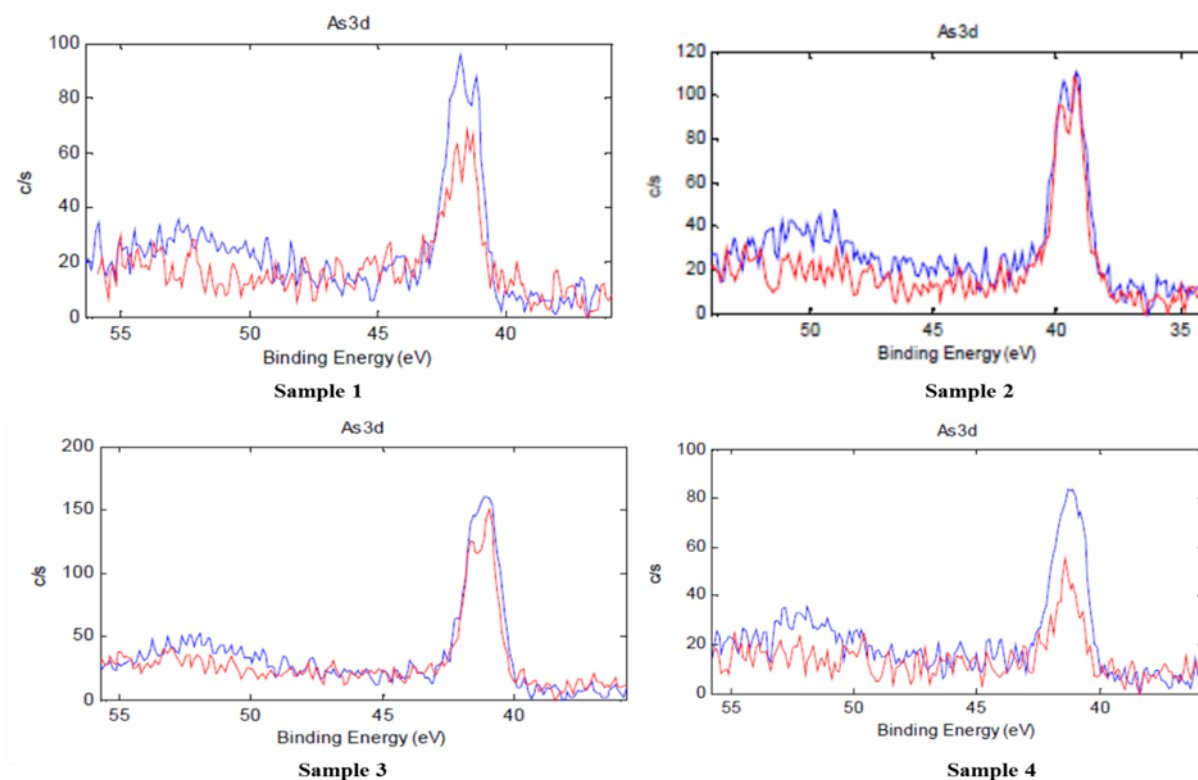

Figure 9: As3d XPS peaks for all 4 samples. Bottom curve represents survey at the surface of sample and top curve survey after 2 minutes of depth profile-penetration of 36 nm

The cyanide-only leach after 3 runs, from which Sample 2 is taken, indicated an increasing degree of 'passivation' with less and less Pt and As leached in each run (Figures 3 and 4). In fact the peak for Sample 2 is closer to the 41.3-41.6 eV associated with As^0 than the other 3 samples. Perhaps this shift from the known range represents an intermediate or transitional state of As compound in which As is in between negative and positive oxidation states. It then follows that this new state of As may actually completely change the structure of the sperrylite at the surface, resulting in a form of sperrylite that is more difficult to leach, which is why in the cyanide-only leaching experiments some Pt leached out and then it stopped. In line with what was postulated earlier, this new phase is of the form $PtAs_{(X)}$ where x is less than 2, and in which both Pt and As tend to more 'net neutral' oxidation states.

Unfortunately, no XPS analysis could be done on the residue sample for the continuous leach experiment. It would have been of considerable interest to understand why a single day of water washing was sufficient to reverse the 'passivation' of the sperrylite, if, as becoming clear from the above analysis, it is likely to relate to the formation of an As depleted surface layer. It is

plausible, but unlikely, that the one-day 'break' would allow As to diffuse back from the bulk mineral into the depleted surface, thus to replenish it and allow again for rapid leaching as the ferricyanide-cyanide solution is re-introduced.

4.4 Electrochemical Study

The presence of ferricyanide significantly enhances the dissolution of sperrylite. The assumption is that it acts as an oxidant of arsenic species present in the mineral. Thus an electron transfer takes place at the mineral surface, which can be studied further with potentiometry tools.

Open circuit potential (OCP) experiments were conducted with a mineral electrode made from a large piece of sperrylite as described in the Experimental section. The freshly polished probe was immersed in solutions of varying amounts of $K_3[Fe(CN)_6]$ in a 5 g/L NaCN solution, more specifically 0.5, 5 and 25 g/L, and rotated at 1600 rpm. The OCP was monitored over 17 hours (Figure 10). All the curves had an identical shape and started at a potential of 205 mV, indicating that the different quantities of ferricyanide used did not have a significant effect on the reaction. The continuous decline of OCP over 17 hours is most likely related to the reduction of ferricyanide at the surface and the concomitant increase in the reduced ferrocyanide species in the batch system, which results in a slowing reduction rate at the surface. As at OCP (which is equivalent to the mixed potential) the rate of reduction must equal the rate of sperrylite oxidation, slower leaching would be expected as OCP drops. A slowing of leaching is indeed observed in the batch system (Figures 5 and 6) and may in part be attributable to the gradual build-up of ferrocyanide in the reactor (although this was not measured independently).
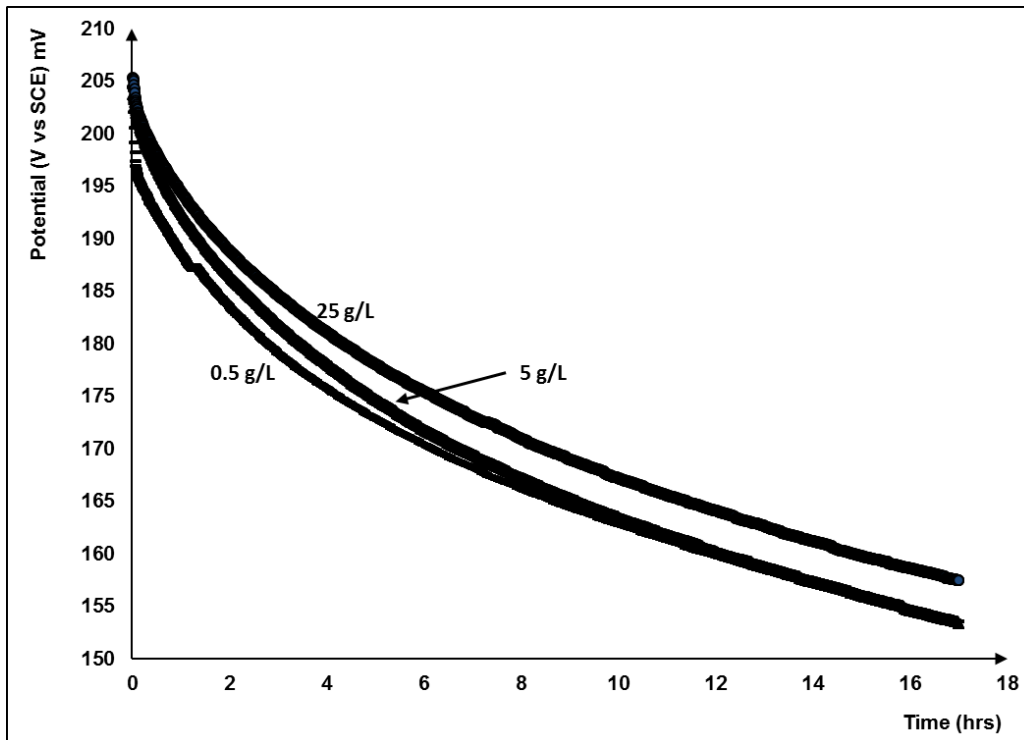
Figure 10: Open circuit potential measurements for 5 g/L NaCN and 0.5, 5 and 25 g/L K₃[Fe(CN)₆] solution at 40°C for 17 hours.

In order to appreciate the response of the sperrylite mineral to an applied oxidation potential, cyclic voltammetry experiments were conducted in cyanide-only solution. This was done so to conduct all electrons released from the anodic dissolution reaction through the electrode wire rather than to the oxidant at the mineral surface and thus make the rate of electron exchange measurable as a current. In the present experiment the voltage was increased from the initial OCP (-180mV in the absence of any ferricyanide) to 450 mV (1) then decreased to -330 mV (2) and increased again to 450 mV (3). The pattern in Figure 11 is such that at higher potentials an anodic reaction is supported, but when the potential is reduced the current drops to near zero as expected, indicating no cathodic reaction. But when the voltage is increased again on the reverse sweep, the current density follows the same direction as the previous downward sweep. The discrepancy between the first and subsequent upsweeps is probably related to a small amount of As released which is oxidised further (As(III) to As(V)).
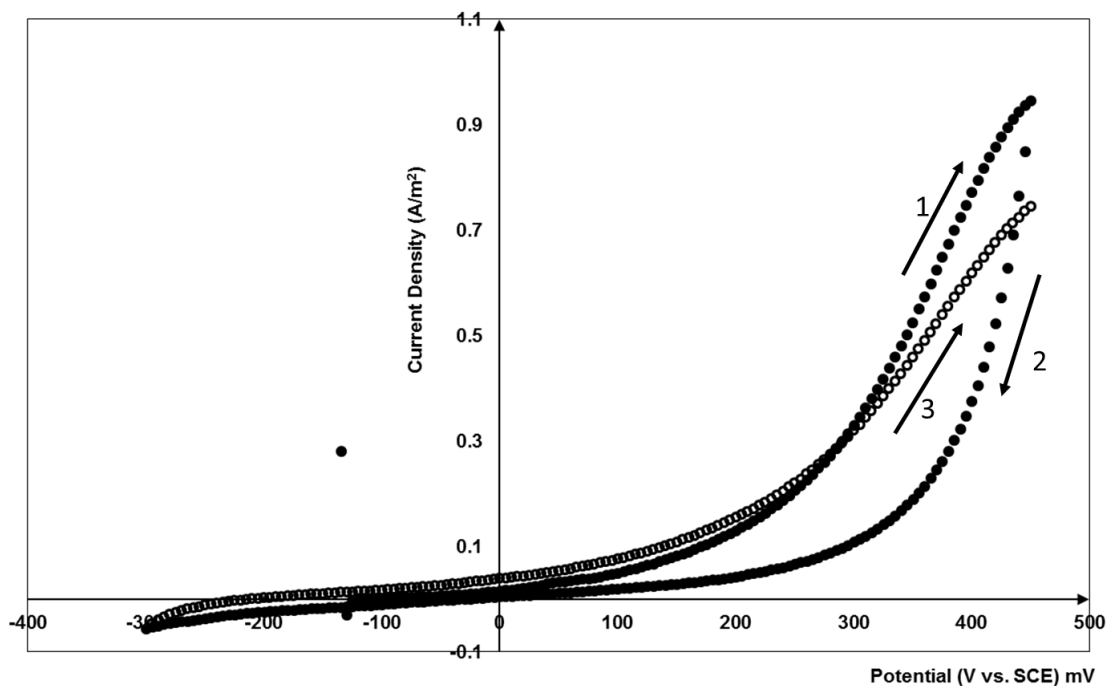
Figure 11: Cyclic voltammogram for sperrylite in 5 g/L NaCN at 40°C between 450mV and -300mV

It is now of interest to monitor the rate of leaching (through the current) at a fixed potential. Although the potential at which OCP was measured was around 205mV for the ferricyanide-cyanide system, it was decided to operate at a higher potential of 380 mV for this test in order to achieve higher oxidation rates (0.8 A/m^2 vs 0.15 A/m^2 at 205 mV, see Figure 11) and ideally release sufficient Pt and As into solution to estimate the specific number of electrons transferred in the dissolution reaction. Thus a chrono-amperometry experiment was run at 380 mV for 2 days. In this experiment again only cyanide solution was used without ferricyanide.
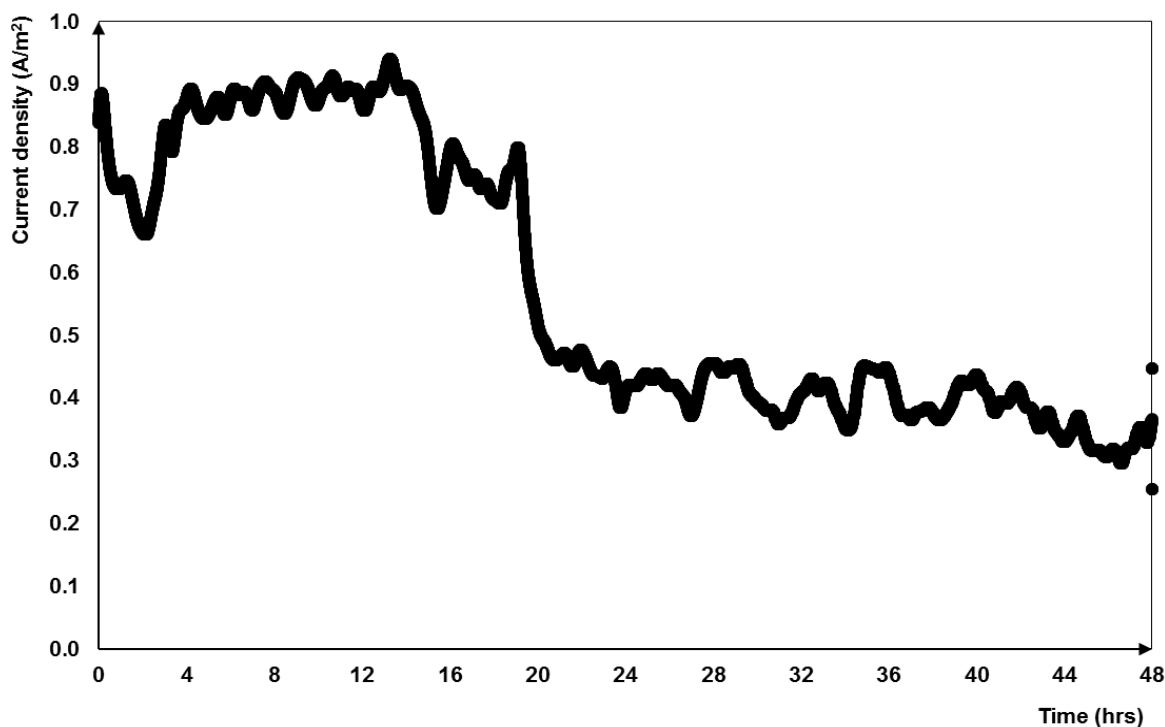
Figure 12: Chronoamperometry for 5 g/L NaCN running at 380 mV at 40C for 2 days
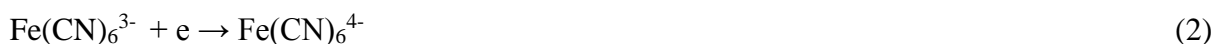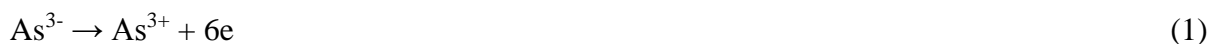
Figure 12 shows the current versus time curve from the experiment. It is noted that the current profile remains very erratic throughout, with significant fluctuations of as much as 20% about the average. The experiment starts around a current density of around 0.85 A/m^2, which compares well with what measured at the operating potential in the potential sweep in Figure 11. In the second half of the first day the current drops relatively suddenly (over about 8 hours) to about half of the earlier current density (around 0.45 A/m^2) and gradually declines further to around 0.35 A/m^2 over the following 24 hours. The sudden drop is peculiar, but tallies with the noticeable levelling-off of the Pt and As leach curves observed in the first runs of the ferricyanide-cyanide leach tests (Figures 5 and 6), which also seem to be attributable to a passivation phenomenon at the sperrylite surface, although it is not as strongly observed in the 2nd and 3rd runs of these experiments.

Unfortunately, even after running for 2 days, the levels of Pt and As in solution were not accurately detectable by ICP-OES. These low levels are not surprising given the extremely low currents (and hence leach rates) in the experiment from the onset and the small surface area of the mineral exposed on the electrode. Without this information it is not possible to proceed with calculating the number of electrons transferred in the dissolution of sperrylite as this would allow conclusions about which oxidation state of As in the solid is oxidised to which in solution.

5.0. Conclusion

The work presented here gives a clear indication that the slow leaching of sperrylite in cyanide can be attributed to a form of passivation. This was observed in tests in which fresh solution was applied after the leaching of Pt levelled off, and with each fresh application less Pt was leached. Without a suitable oxidant to oxidise As in sperrylite to a higher oxidation (and hence more soluble) state, an eventual build-up of As results at the surface of the mineral, which acts as a passivation layer causing slow leaching of Pt. XPS analysis further suggested that the As remaining behind was in an oxidation state closer to 0, suggesting that in a cyanide-only system the limited oxidant does not completely oxidise As but leaves it in an intermediate/transitional oxidation state. Further, this may change the entire sperrylite structure at the surface, forming a less cyanide soluble compound of the form $PtAs_{(X)}$ where x is less than 2.

Identical leaching tests conducted with the addition of ferricyanide as an oxidant conclusively showed that the presence of ferricyanide significantly improved the leaching Pt and As, leaching 12-16 times more than what was leached in the experiments that used only cyanide solution. It is believed that the ferricyanide oxidises the part of the As in sperrylite that is in a lower oxidation state to a higher oxidation state thus breaking the chemical bonds of the sperrylite to release Pt into solution to be complexed with cyanide. In doing so the ferricyanide is reduced to ferrocyanide, representing a cathodic reaction to the anodic reaction of the As oxidation. The part of the As that is in lower oxidation state is most likely in the -3 state. This is the most common lower state of the As and is most likely oxidised to +3, rendering it soluble. The steps of this mechanism are represented by the following equations:

$$As^{3-} \rightarrow As^{3+} + 6e \tag{1}$$

$$Fe(CN)_6{}^{3-} + e \rightarrow Fe(CN)_6{}^{4-} \tag{2}$$

$$Pt^{2+} + 4CN^- \rightarrow PtCN_4{}^{2-} \tag{3}$$

However, a phenomenon which is yet to be fully explained is the fact that washing and contacting the mineral with fresh solution can reverse the passivation, at least partially in the cyanide-only system, and fully in the ferricyanide-cyanide system. It is most probable that this washing step will allow desorption of an inhibiting species on the surface of the sperrylite rather

than dissolution of a reaction product not soluble in the cyanide solutions. This needs to be investigated further, as any suggestion as to what adsorbs and onto what phase would be entirely speculative at this stage. What is peculiar to note, however, is that this adsorption occurs only very gradually (as opposed to the apparent desorption during water washing), and may in fact be linked to the gradual alteration of the surface during leaching, i.e. a phase conducive to the postulated adsorption reaction is formed only gradually as the reaction proceeds. There is a tentative indication that this phase this could be an altered and possibly more metallic mineral species of the form $PtAs_{(x)}$, where x is less than 2.

Regardless of the mechanisms, the results from this study clearly show that a combination of ferricyanide-cyanide is a potential solution to the low Pt extractions using cyanide-only in Platreef ore heap leaching. It should be evaluated further using laboratory column and pilot scale test work.

6.0. References

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