Electrochemical studies of gold ore processing wastewater containing cyanide, copper, and sulfur compounds

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Abstract

The electrochemistry of real gold ore processing wastewater solutions from copper sulfide containing gold ore has been investigated. Analysis shows that the wastewater contains a range of sulfur compounds in various oxidation states from sulfide to sulfate. The electrochemical characteristics of the gold ore processing wastewater were evaluated using rotating disk, cyclic voltammetric, polarization and preparative electrolysis studies. The solutions show clear differences versus synthetic alkaline copper cyanide solutions. The copper cyanide/copper oxide catalysis normally seen in synthetic alkaline copper cyanide solutions is strongly inhibited. Two components of the wastewater solution identified as inhibiting the copper cyanide/copper oxide catalysis are copper sulfide complexes and thiocyanate. The inhibition of the copper cyanide/copper oxide catalysis appears to have an initiation time possibly related to the accumulation of copper-sulfur compounds at the electrode surface. The passivated surface is still able to oxidize cyanide, though at a maximum rate that corresponds to the limiting current for free cyanide assuming 1 electron per cyanide. The lack of the copper oxide coating that typically forms during oxidation of synthetic alkaline copper cyanide solutions, plus possibly the presence of various sulfur compounds, results in corrosion at higher anodic potentials when stainless steel is used as an electrode. However, stainless steel can be successfully used as an electrode material to treat the solutions if the potential is carefully controlled.

1. Introduction

Cyanide has been widely used in the gold mining industry since the late 1800s to dissolve gold from pulverized ore [1]. The gold is leached from the ore using oxygen saturated alkaline cyanide solution, from which it is recovered using activated carbon. In some gold mines, there is a high content of copper related to the presence of Cu_2S (chalcocite) and CuS (covellite). During the leaching process, the copper dissolves with the gold in the alkaline cyanide solution. In addition, the sulfide is oxidized to sulfite, sulfate, thiocyanate and thiosulfate in the presence of oxygen and cyanide. Consequently, after the gold is recovered, the wastewater usually contains a high concentration of copper, cyanide and sulfur compounds.

The traditional wastewater treatment method involves holding the solutions in large lagoons to allow the slow breakdown of the cyanide [1]. Once the cyanide is destroyed, the metal ions precipitate and the supernatant can be neutralized and discharged. This storage of large quantities of wastewater represents a cost both in terms of infrastructure and in terms of potential liability in the event of an accidental release [2]. It is worth noting that such accidental releases often include re-suspended metal sludges from the lagoon bottom that can have a more long-term impact on the environment than the cyanide solutions. Also, the metal sludges in the lagoons represent problems even after the mine is closed [3].

Alternative treatment methods need to be able to handle large volumes of low concentrations of metal cyanide wastewater at low cost. Many methods have been proposed including alkaline chlorination, biological treatment, Caro's acid, the Inco SO_2/air process and hydrogen peroxide [4, 5]. Of these, the two methods that have been most successfully applied are the Inco SO_2/air process and hydrogen peroxide treatment. The Inco SO_2/air process [6, 7] involves using SO_3^{2-}, which reacts together with oxygen and copper cyanide complexes resulting in cyanide oxidation and, in the presence of sufficient base, the formation of cyanate. While this process works well, it requires continuous addition of chemicals and careful process control to keep the chemistry in its optimum balance. At the end of the

reaction, copper precipitates out as copper hydroxide. Hydrogen peroxide treatment involves using hydrogen peroxide to oxidize copper cyanide complexes, leading to the formation of cyanate [8].

Both the Inco and hydrogen peroxide approaches actually require copper cyanide complexes for catalysis. Thus, copper must be present at an appropriate concentration for both methods to work properly. For wastewater with a high concentration of sulfur compounds, additional oxidation will be needed to complete the treatment (especially expensive if hydrogen peroxide is being used). Finally these methods will result in metal oxide, hydroxide and/or sulfide sludge products that require disposal.

Electrochemical methods for treating copper cyanide solutions have been investigated by numerous researchers [9–20]. In electrochemical methods, while cyanide is oxidized to cyanate at the anode, copper is recovered at the cathode avoiding copper precipitation. While electrochemical treatment would require a higher capital cost, it should, by avoiding consumption of chemicals, be able to offer a lower operating cost.

The electrochemical oxidation of cyanide to cyanate is also catalyzed by copper. In our previous work, no oxidation current is found for alkaline sodium cyanide at the glassy carbon electrode at potentials below oxygen evolution [20]. With copper present, at low overpotential, and without sufficient hydroxide [20] the reaction mechanism for cyanide oxidation has been suggested in the literature [13, 21].

$$[Cu(CN)_3]^{2-} \rightleftharpoons [Cu(CN)_3]^- + e^- \tag{1}$$

$$2[Cu(CN)_3]^- \rightleftharpoons [Cu_2(CN)_6]^{2-} \tag{2}$$
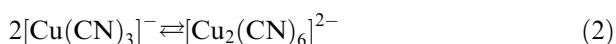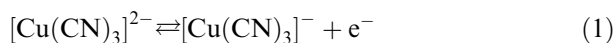
The copper(II) complex, $[Cu_2(CN)_6]^{2-}$, decomposes to release cyanogen and $[Cu(CN)_2]^-$.

$$[Cu_2(CN)_6]^{2-} \rightarrow 2[Cu(CN)_2]^- + (CN)_2 \tag{3}$$
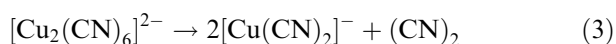
The $[Cu(CN)_2]^-$ can then pick up a free cyanide to regenerate $[Cu(CN)_3]^{2-}$.

$$[Cu(CN)_2]^- + CN^- \rightleftharpoons [Cu(CN)_3]^{2-}$$
$$K_{eq} = 2.0 \times 10^5 \text{ M}^{-1} [22] \tag{4}$$
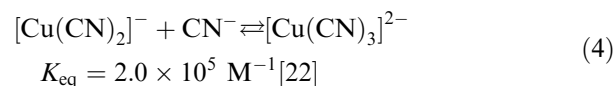
It is also thought that $[Cu(CN)_4]^{3-}$ reacts by a similar route, which would require the loss of a cyanide ligand from the complex before forming $[Cu_2(CN)_6]^{2-}$, however the exact steps remain to be determined. This mechanism was proposed as a solution reaction [21], though others feel that the predominant path involves a surface adsorbed intermediate [13, 20]. The cyanogen produced then reacts with hydroxide to produce cyanate [23], with the overall reaction shown below.

$$(CN)_2 + 2OH^- \rightarrow CN^- + CNO^- + H_2O \tag{5}$$
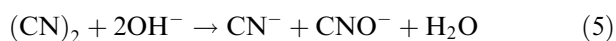
For low hydroxide concentrations (where the reaction will proceed more slowly) or high mass transport rates (where the boundary layer thickness is small), most of the cyanogen will diffuse out to the bulk before reacting. Thus, only one electron is transferred from each reacted cyanide (equations 1 to 3). At higher hydroxide concentrations or lower mass transport (thicker boundary layer), more of the cyanogen will be decomposed before diffusing far from the electrode. This will release free cyanide close to the electrode for further oxidation. In the extreme case, this will result in 2 electrons per molecule ($z_{eff} = 2$) for complete conversion of cyanide to cyanate close to the electrode surface. An initial approach to estimate these effects has been presented by Hofseth and Chapman [14], though it does not include the full complexity of the cyanogen reaction mechanism as described elsewhere [23].

At higher overpotentials with sufficient hydroxide [20], an autocatalytic reaction that results in the formation of a black deposit, identified as copper(II) oxide (CuO), occurs at the anode [9, 12, 18] (with some copper hydroxide also associated with the film) [24]. This deposit acts as a heterogeneous catalyst for the oxidation of cyanide [9] and for a range of organic compounds [24]. This is thought to be due to a surface copper(III) intermediate [9, 17, 20]. Work investigating the electrochemistry of copper in alkaline solutions has shown the presence of Cu^{3+} at around 0.65 V vs. Hg/HgO using a RRDE [25], related to a voltammetric wave observed just before the onset of oxygen evolution [9, 26]. Under these conditions (where CuO is present) the reaction of copper cyanide complexes is essentially complete (and, with further oxidation, cyanate is even oxidized to nitrate [20]).

$$[Cu(CN)_3]^{2-} + 8OH^- \rightarrow 3OCN^- + CuO + 4H_2O + 7e^- \tag{6}$$
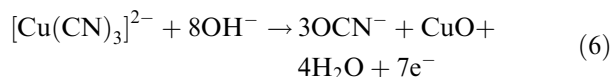
Most previous work on electrochemical treatment has focused on synthetic copper cyanide solutions with no sulfur compounds. However, to our knowledge, there haven't been any detailed studies done on industrial alkaline copper cyanide solutions resulting from leaching of sulfide ores. In investigating the electrochemical treatment of industrial alkaline copper cyanide wastewater from gold ore processing, we have found that the industrial solution gives very different results versus a synthetic solution. The purpose of this work is therefore to examine the electrochemistry of industrial wastewater from a gold ore processing operation that handles copper sulfide containing ore. In particular, the effect of the sulfur compounds on the electrochemical process is investigated and discussed in this paper.

2. Experimental

CuCN (99.99%), Cu₂S (102.5% based on Cu content) and NaCN (97.9%) were obtained from Aldrich and used without further purification. Standardized 1.000 N sodium hydroxide and 18 MΩ ultrapure water were

used to prepare all solutions. Copper cyanide synthetic solution was prepared from CuCN, NaCN and 0.1 M sodium sulfate. A new generation of synthetic solution was prepared by stirring Cu_2S, NaCN and $Ca(OH)_2$ under air in purified water for 20 h. Industrial gold mine wastewater was obtained from Technologies ECT5 and consisted of samples from the end of the gold recovery process, before entering the lagoon.

A conventional 3-electrode electrochemical cell was used for all experiments. The working electrode is a glassy carbon with a surface area of 0.196 cm^2. Rotating disk electrode (RDE) experiments were controlled by the EG&G PARC Model 616 RDE apparatus. Unless otherwise stated, a rotation rate of 2500 rpm and a scan rate of 2 mV s^{-1} were used. The auxiliary electrode was a platinum gauze. Electrode potentials are reported versus a Hg/HgO/0.1 M NaOH reference electrode. All electrochemical measurements were performed on a Solartron 1287 Interface.

Preparative electrolyses were also performed using a small flow-by type cell with three-dimensional electrodes, diagrammed in Figure 1. The electrodes were made of spot welded stacks of 0.142 cm thick 8×8 mesh screen. The screen was fabricated of 0.028 in. dia. type 304 stainless steel wire, yielding an approximate specific area of 9.9 cm^{-1} and 57% void volume. This gave a cathode area of 49 cm^2 and a total anode area of 81 cm^2. (The higher anode area was chosen because there is more cyanide to be removed in comparison to copper). The cell voltage was controlled using a power supply. Readings of the anode potential were made using a Hg/HgO/0.1 M NaOH reference electrode just ahead of one anode and the cell voltage was adjusted to maintain the anode potential within a desired range. A peristaltic pump was used to provide a flow of about 30 ml/min., which gave a superficial velocity in the cell of around 0.1 cm s^{-1}.
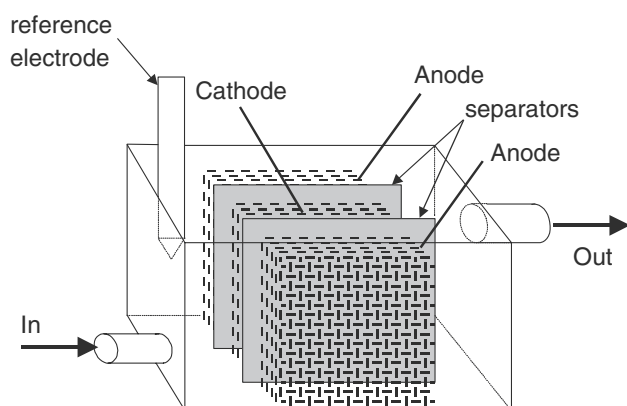

Fig. 1. A diagram of the test cell. The cell used one cathode between two anodes with the cathode consisting of 6 layers of 2.5 cm $\times$ 2.5 cm type 304 stainless steel screen spot welded together, while the anodes both used 5 layers. Readings of the anode potential were made using an Hg/HgO/0.1 M NaOH reference electrode just ahead of one anode.
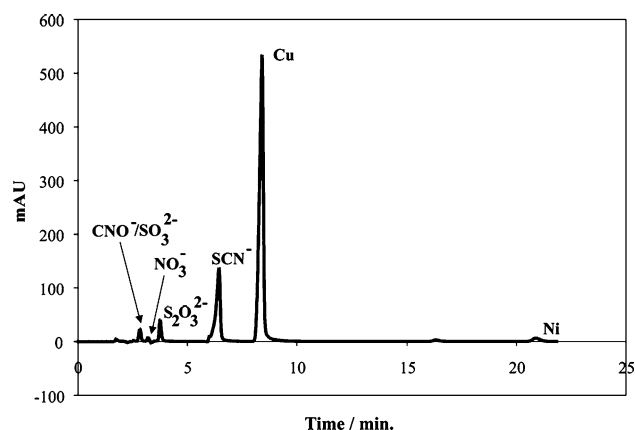

Fig. 2. A typical HPLC chromatogram for a gold processing waste-water sample.

The composition of the copper cyanide solution was analyzed by reversed-phase ion-interaction HPLC (see Figure 2) and cyanide ion-selective electrode. The HPLC technique was modified from the method described by Fagan et al. [27]. Generally speaking, the stationary phase was a 15 cm Supelcosil LC-18-DB from Supelco. The mobile phase consisted of an ion-pairing agent (tetrabutylammonium hydrogen sulfate), a buffer (phosphate salts), 10 mM potassium cyanide and 20% of acetonitrile. The IPC-A obtained from Alltech or Waters was used as the source of the ion-pairing agent and phosphate buffer. The pH of the mobile phase was adjusted to 7.3–7.4 by adding phosphoric acid. The cyanide in the mobile phase improved the quality of the metal-cyanide complex peaks by reducing the dissociation of the complex. The concentration of copper was determined by comparing to a standard solution. Random sampling of the copper cyanide solutions by atomic absorption spectroscopy gave the same results within experimental error. In addition, cyanate, nitrate, sulfite, thiosulfate and thiocyanate were also determined. No significant unknown peaks were observed. However, under our operating conditions, the sulfite signal coincides with the cyanate and the two signals could not be resolved. Corrosion of the stainless steel anode can be detected from a nickel peak from the HPLC.

The cyanide concentration was measured using an Orion 9606 combination cyanide ion selective electrode (ISE). Samples (0.1 ml) were added into identical glass vial and stir bar sets containing the 6 ml of 0.5 M NaOH. To provide uniform mass transport, the electrode was inserted in the same position in each vial, and the sample agitated throughout the measurement with a magnetic stirrer set at a controlled stir rate. The electrode was calibrated before and after each set of samples using solutions made with standardized 1000 ppm cyanide solution from Labchem Inc.

The total cyanide concentration was estimated from the copper concentration and the cyanide concentration measured using the ISE. The ISE works by
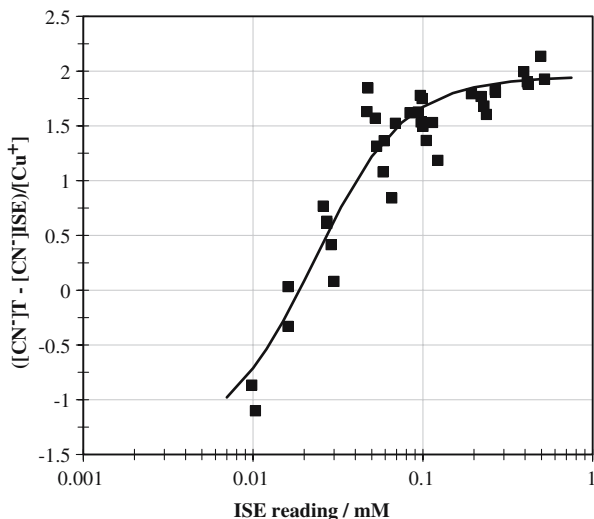
Fig. 3. Calibration curve for the correction factor for the cyanide ISE with copper present, showing the fit obtained with the α_1 and α_2 empirical constants.

measuring the dissolution current for silver iodide in the presence of free cyanide. This results in a local displacement of the copper cyanide equilibria, leading to partial dissociation of the copper cyanide complexes, releasing additional cyanide. This introduces an additional factor in the ISE reading that depends on the amount of copper present and its degree of dissociation. This degree of dissociation was estimated using a semi-empirical approach based on a method described previously [28]. This allows the total cyanide ($[CN^-]_T$) to be estimated using the ISE reading ($[CN^-]_{ISE}$), the copper concentration ($[Cu]_T$), and a correction factor associated with the amount of copper (ε):

$$[CN^-]_T = [CN^-]_{ISE} + [Cu]_T \varepsilon \qquad (7)$$

where:

$$\varepsilon = \frac{1.96\alpha_1 CN_{ISE} + 1.0\alpha_2 - \frac{3}{2CN_{ISE}}}{\alpha_1 CN_{ISE} + \alpha_2 + \frac{1}{CN_{ISE}}}$$

and α_1 and α_2 are empirical constants found in this work to be equal to 1.6×10^3 mM^{-2} and 2.1×10^1 mM^{-1} respectively.

The difference between total cyanide and measured cyanide, normalized for the copper concentration, (ε), is shown in Figure 3 for a series of standard solutions measured at various times over the course of this work. This difference is basically the average number of cyanide ligands held per copper, and thus unavailable to be measured by the ISE. The fit obtained with equation 6 is also plotted and gives a standard error in the estimate of ε of 0.28. Further verification of this approach was obtained by random testing of various experimental samples for total cyanide using total cyanide distillation, which gave comparable results, within experimental error.

3. Results and discussion

3.1. *Analysis of gold mine wastewater*

The industrial solutions used were collected over a period of time from a single gold ore processing operation. The results of the solution analysis by HPLC and cyanide ion-selective electrode are shown in Table 1. As discussed in the experimental section, sulfite and cyanate co-eluted and so they could not be quantified. In any case, sulfite and cyanate slowly decompose in alkaline solutions making quantitative analysis problematic. Also, as described in the experimental section, the total cyanide concentration is estimated from the $[Cu^+]$ determined from HPLC and the $[CN^-]$ measured by ISE. The results were comparable to values obtained by total cyanide distillation (the Midi method). However, one should point out that the sulfur compounds can interfere with the two methods of cyanide measurement. For total cyanide distillation, an overestimation of cyanide concentration is obtained when thiocyanate is present. And while the presence of thiocyanate has no effect on the cyanide measurement by ISE, a small amount of sulfide can significantly affect the measurement. However, because of the improved speed and convenience and the high concentration of thiocyanate in the mining solution samples, the ISE method was used for most of the work in this paper.

Analyzing the solutions, we have found that the samples collected at different times showed significant variations. This is probably due to the variations in the feed ore (and therefore processing conditions) from day to day, as well as the different ages of the samples. Variations in the ore (e.g. the amounts of chalcocite and/or covellite) will impact the starting amounts of copper and sulfur. The cyanide concentration will be adjusted in the process to obtain good recovery of the gold. Finally, the sparging of oxygen in the leaching process will result in the slow oxidation of the starting chemicals, producing cyanate and nitrate as well as a range of sulfur compounds of various oxidation states, leading eventually to sulfate. While the amount of copper varies slightly, with sample #1, #2 and #3 being lower than #4 and #5, the total cyanide/copper ratio is relatively constant around 3.1 to 3.6.

A few samples were also measured by atomic adsorption (AA) (see Table 2) and one sample was analyzed by an external laboratory using induced coupled plasma

Table 1. Composition of industrial wastewater collected over different periods of time (Concentrations in mM)

Sample	$[Cu^+]$	$[CNO^-] + [SO_3^{2-}]$	$[NO_3^-]$	$[SCN^-]$	$[S_2O_3^{2-}]$	$[CN^-]_{total}$
#1	4.0	Present	0.09	6.8	1.5	12.4
#2	4.2	Present	0.08	6.0	2.1	14.0
#3	4.1	Present	0.10	6.1	1.9	13.2
#4	6.4	Present	0.25	5.1	1.1	21.3
#5	5.6	Present	0.17	7.5	0.2	20.3

Table 2. AA analysis of sample solutions

Sample #	Pb/ppm	Fe/ppm	Ni/ppm	Cr/ppm
2		0.5	0.2	
3		0.4	0.2	
4	< 0.1	0.3	0.2	< 0.1
5		< 0.1	0.3	

Table 3. ICP-MS analysis of Sample #4

| Element	mM	ppm
Cu	6.5	410
Zn	0.21	14
Ni	0.002	0.1
Fe	< 0.009	< 0.5
K	1.9	75
Na	36	830
Ca	15	590
*SO_4^{2-}	15.6	1500

*Determined by sulfate ion-selective electrode.

Fig. 4. Electrochemistry of copper cyanide synthetic solution and industrial wastewater on rotating glassy carbon electron at 2500 rpm with a scan rate of 2 mV s^{-1}. The copper cyanide synthetic solution has 5.5 mM of Cu$^+$, 21.6 mM CN$^-$ and 20 mM of OH$^-$. The industrial wastewater has 6.4 mM of Cu$^+$, 21.3 mM of CN$^-$ and 27 mM of OH$^-$ (Sample #4).

– mass spectroscopy (ICP-MS) and sulfate ion-selective electrode (see Table 3). The samples tested all show low concentrations of iron and nickel. The presence of trace iron is not surprising as the feed ore could contain iron and the steel balls in the ball mill used to crush the ore are replaced on a regular basis due to attrition.

The ICP-MS analysis shows substantial amounts of sodium and calcium likely from the sodium cyanide and lime used in the leaching process. Lime is added to keep the mining solution basic to prevent the formation of hydrogen cyanide gas. The pH of the industrial wastewater is typically in the neighborhood of 13. There is also a significant concentration of sulfate, being the end product of the oxidation of the starting sulfur compounds.

Despite their variations in composition, electrolysis of the solutions showed similar overall cyanide and copper removal rate constants, which were much lower than those for synthetic solutions. This prompted a more detailed investigation of the electrochemistry of the industrial wastewater

3.2. *Electrochemistry of industrial gold mine wastewater*

The cyclic voltammograms of the synthetic copper cyanide solution and a typical industrial solution (Sample #4) are shown in Figure 4. While the two solutions have comparable concentrations of copper, total cyanide and hydroxide, the electrochemistry is very different. As discussed in a previous paper [20], different types of reactions are believed to occur depending on the electrode potential and the solution composition at the electrode surface. At low overpotentials, reactions 1 through 4 occur. As such reactions proceed, free cyanide, hydroxide and [Cu(CN)$_3$]$^{2-}$ are consumed and [Cu(CN)$_2$]$^-$ is generated at the electrode surface. With sufficient overpotential, and if hydroxide is available at
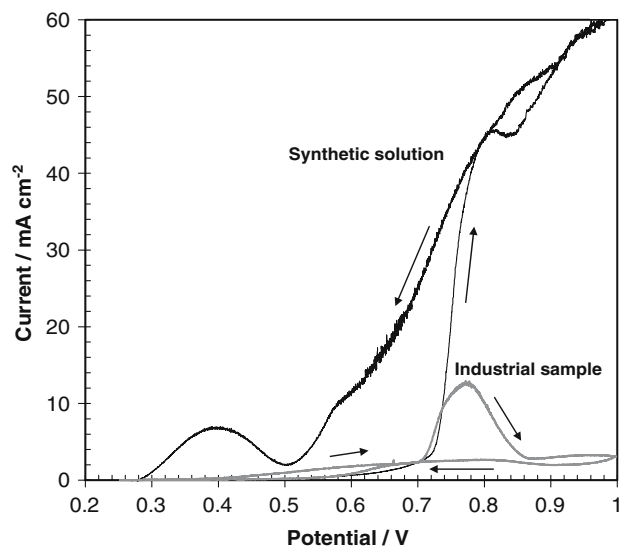
the electrode surface (i.e. it has not been excessively depleted by reaction 5), then further oxidation occurs leading to the formation of copper oxide. Once formed, the copper oxide layer is catalytic, causing the reaction to accelerate in an autocatalytic manner. Note the very rapid increase in current for the synthetic solution curve starting around 0.7 V, and the much higher current on the reverse sweep (i.e. once CuO has been formed on the electrode surface). With the industrial solution, the current begins slightly higher, then starts to increase after 0.7 V. However, it peaks around 13 mA cm^{-2} and no increased activity is observed on the return sweep. Indeed, on cycling a platinum electrode in the industrial solution, only a brownish black tarnish was observed (rather than the black copper oxide deposit normally found).

The expected currents for the various reactions presented in the introduction can be estimated using the Levich equation [29] and the resulting values are shown in Table 4. For reaction 1, one can estimate a limiting flux for [Cu(CN)$_3$]$^{2-}$. If the only product is cyanogen, the z$_{eff}$ would be 1. If, however, the cyanogen rapidly decomposes to release free cyanide that regenerates a [Cu(CN)$_3$]$^{2-}$ from a [Cu(CN)$_2$]$^-$ close to the electrode surface, a z$_{eff}$ closer to 2 might be observed. One can also calculate a maximum flux for the free cyanide, which could also regenerate [Cu(CN)$_2$]$^-$ possibly also having a z$_{eff}$ between 1 and 2. (Note that the kinetics of steps 2 to 5 would need to be very fast to actually achieve z$_{eff}$ = 2). Without further catalysis these two reactions would result in the limiting current referred to in Table 4 as the "non-CuO" related reactions. At this limit, the local concentrations at the electrode surface of free cyanide and [Cu(CN)$_3$]$^{2-}$ would

Table 4. Predicted limiting currents for different reaction schemes

Reaction	Diffusing species	z_{eff}	$i_{limiting}/$ mA cm^{-2}
copper cyanide oxidation	$[Cu(CN)_3]^{2-}$	1	6.5
		2	13.0
free cyanide oxidation	CN^-	1	3.3
		2	6.6
Total of non-CuO related reactions		1	9.8
		2	19.7
Complete oxidation to CuO	$[Cu(CN)_3]^{2-}$	7	52.3
	CN^-	2	

The value of z_{eff} depends on whether the cyanogen decomposition (reaction 4) releases free cyanide close to the electrode surface ($z_{eff} = 2$) or only slowly in the bulk solution ($z_{eff} = 1$). The diffusion coefficients used were 2.08×10^{-5} cm^2 s^{-1} for cyanide [30], and 1.08×10^{-5} cm^2 s^{-1} for $[Cu(CN)_3]^{2-}$ [31] and a kinematic viscosity of 0.01 cm^2 s^{-1} [29]. (Assumed 6.4 mM copper as $[Cu(CN)_3]^{2-}$, hence 2.1 mM as free cyanide).

be zero, with the main species present being $[Cu(CN)_2]^-$. Further oxidation of $[Cu(CN)_2]^-$, leading to copper oxide, would result in an overall reaction of $[Cu(CN)_3]^{2-}$ as written in equation 6. This reaction, plus the oxidation of the free cyanide, would result in the "complete oxidation" limiting current in Table 4.

It can be seen that for the synthetic solution (which has roughly similar concentrations of key species) that complete oxidation is achieved. (The additional current beyond about 0.9 V is due to oxygen evolution from excess OH^- [20]). For the industrial solution, while there appears to be an onset of CuO catalyzed oxidation at 0.7 V, it becomes inhibited resulting in a limiting current around 2.6 mA cm^{-2} (this plateau current is rotation sensitive, hence a limiting current, as will be shown later). Even in our previous work, where solutions with insufficient hydroxide to allow formation of CuO were tested, limiting currents near those predicted for the total of non-CuO related reactions with $z_{eff} = 1$ (corresponding to 9.8 mA cm^{-2} in Table 4) were found [20]. Thus, some species in these industrial solutions is causing a dramatic change in the reaction pathways.

3.3. Search for the interfering compound

Work was therefore carried out where different possible interfering species were added to the synthetic solution to try to identify the problem compound. The influences of some sulfur compounds on the electrochemistry are shown in Figure 5 (using concentrations similar to those found in the wastewater samples). Thiosulfate and sulfite have only minor effects on the voltammetry. For both of these species, higher currents are observed at lower potentials and the onset of rapid, CuO catalyzed, reaction occurs slightly earlier. This might be due to the concurrent oxidation of thiosulfate and sulfite. In the case of thiocyanate, however, the initial currents are lower, the onset of rapid reaction occurs later, and the catalytic reaction rate is not sustained, with the current decreasing to values around 15 mA cm^{-2}. While this result is significant, the
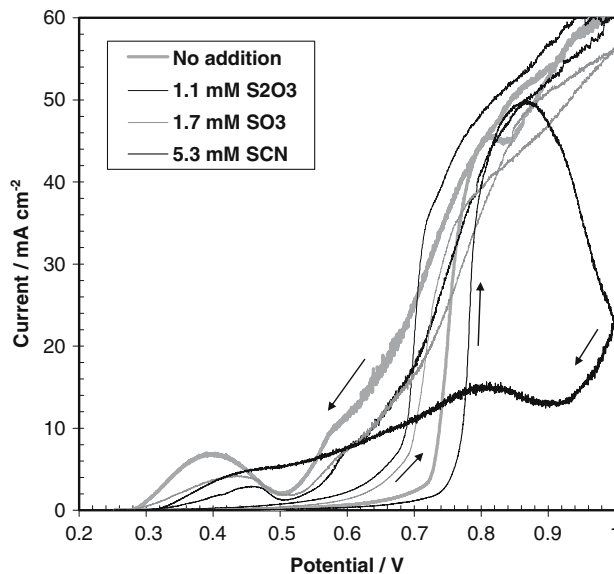

Fig. 5. Electrochemistry of copper cyanide synthetic solutions with addition of 5.3 mM of thiocyanate, 1.1 mM of thiosulfate or 1.7 mM of sulfite on rotating glassy carbon electrode at 2500 rpm with a scan rate of 2 mV s^{-1}. All solutions contain 5.5 mM of Cu^+, 21.6 mM of CN^- and 20 mM of OH^-.

suppression of cyanide oxidation is not as severe as found in the wastewater solution with a similar thiocyanate concentration. The copper in the wastewater originates from the leaching of copper sulfides by the alkaline cyanide solution. Thus, while most of the sulfide is oxidized to thiosulfate, thiocyanate, sulfite and sulfate, there might be some remaining sulfide, possibly associated with the copper cyanide complexes, that is difficult to be oxidized.

Therefore, a synthetic solution was prepared from Cu_2S by stirring a solution of sodium cyanide, calcium hydroxide and copper(I) sulfide for 20 h. The resulting solution was filtered and the filtrate was analyzed. There was 5.3 mM of copper, 19 mM of total cyanide, 0.6 mM of thiocyanate and 0.1 mM of thiosulfate. The concentrations of copper, cyanide and hydroxide in the new synthetic solution are comparable to the wastewater solution though there is a higher concentration of sulfur compounds in the wastewater solution. The synthetic solution was studied on the rotating glassy carbon electrode and the results are shown in Figure 6, compared to the industrial wastewater solution. Even though the thiocyanate concentration is lower (compared to Table 1 and Figure 5), the cyanide oxidation is strongly suppressed with a limiting current of only 5 to 6 mA cm^{-2}. This suggests that sulfide is also responsible for the low activity for cyanide oxidation in the industrial solution. The limiting current in the Cu_2S based solution is still higher than the limiting current with the industrial wastewater solution. Thus, both sulfide and thiocyanate can inhibit the cyanide oxidation reaction.

As might be expected, the results cannot be reproduced by the addition of sodium sulfide into the copper cyanide synthetic solution. The sodium sulfide is quickly
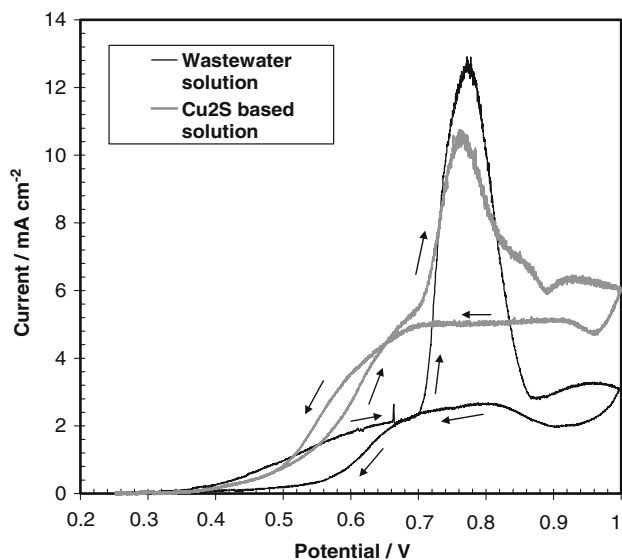
Fig. 6. Electrochemistry of new synthetic solution from Cu_2S on rotating glassy carbon electrode at 2500 rpm with a scan rate of 2 mV s^{-1}. The new synthetic solution has 5.3 mM of Cu^+, 19 mM of CN^- and 22 mM of OH^-.

Fig. 7. The effect of sweep rate on the voltammetry of the wastewater solution (sample #4) at the glassy carbon electrode.

oxidized to other sulfur compounds before interacting with the copper cyanide complexes in the synthetic solution (it is a weaker ligand than cyanide [32]). To achieve the observed suppression of cyanide oxidation one must start with copper(I) sulfide. This suggests that the reaction of cyanide with copper(I) sulfide may give a series of copper cyanide complexes in equilibrium with sulfide that stabilize the sulfide (similar compounds have been described elsewhere [33]). These sulfur compounds not only decrease the eventual limiting current below the values for non-CuO catalyzed cyanide oxidation (equations steps 1 to 4), but also, after a short delay, they inhibit the CuO catalysis.

3.4. The reaction inhibition phenomena

The inhibition of the cyanide oxidation was found to vary with the sweep rate and the electrode rotation rate. The change in the polarization curves with sweep rate is shown in Figure 7. It can be clearly seen that the reaction inhibition (i.e. the point at which the current collapses, producing a peak) is not solely dependent on potential, but rather there is some time dependence. (From the inflection point in the rising current (after 0.7 V) to the peak current corresponds to 29 s for the 2 mV s^{-1} curve, 38 s for the 5 mV s^{-1} curve, and greater than 27 s for the 10 mV s^{-1} curve.) Thus, there may be some period of time or some amount of reaction required before the sulfur compounds accumulate enough to poison the CuO catalyst. The exact mechanism of the catalysis leading to CuO is unknown. The overall reaction (equation 6) likely involves intermediate copper complexes containing cyanide and hydroxide ligands (possibly similar to the Cu(III) complexes reported for hydrogen peroxide driven copper cyanide oxidation [8, 34]). Once started, these reactions continue
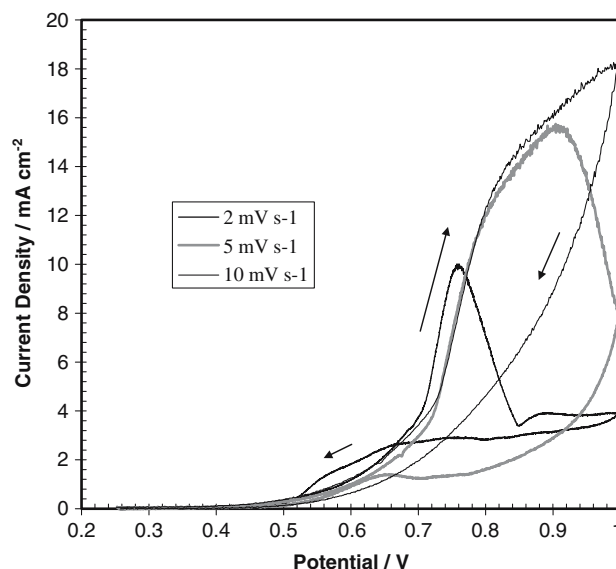
on the surface of a CuO deposit, which progressively thickens on the electrode. Thus, the presence of sulfide containing copper complexes and thiocyanate (a competing ligand) might interfere with the formation of the intermediates needed to achieve the autocatalytic copper cyanide oxidation.

Other experiments have shown that, for a given solution, both the peak current and limiting current increased with the square root of the rotation rate. The observation that the peak current is not constant with rotation rate would tend to indicate that there is not a fixed amount of inhibiting compounds required to de-activate the electrode. One possibility is that there is a certain amount of inhibiting compound per copper required. It is also interesting to note that the limiting current is of a similar value to the estimated limiting current for free cyanide using $z_{eff} = 1$. However, free cyanide, by itself, is essentially unreactive at the glassy carbon electrode [20]. Thus, while the presence of thiocyanate and copper sulfide complexes inhibits the formation of a catalytic CuO coating (and also possibly reactions 1 and 2), the brown tarnish that is observed may still be capable of catalyzing the oxidation of free cyanide.

3.5. Electrode materials

Experiments were also carried out using different electrode materials, with a set of results shown in Figure 8. With synthetic solutions, little difference is seen between electrode materials once they are coated with CuO (other than those due to coating adhesion). The onset of the CuO related cyanide oxidation reaction does change slightly with electrode material and even sometimes with the same electrode, thought to be due to variations in the electrode cleaning [20]. With the wastewater solutions, the results show the onset of
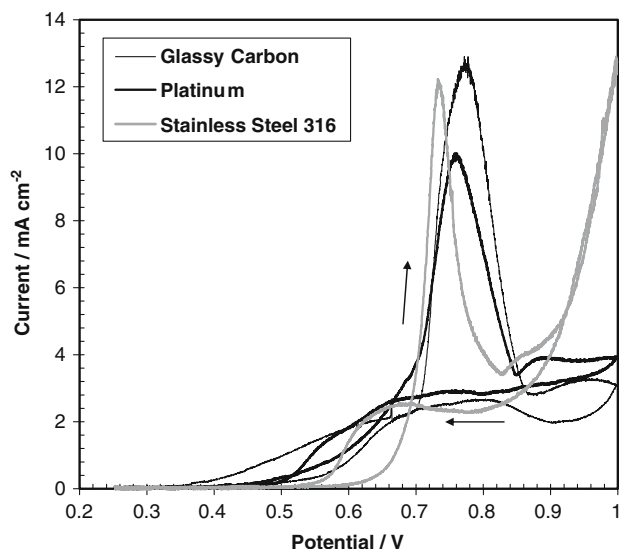
Fig. 8. Electrochemistry of industrial wastewater Sample #4 on different rotating electrodes at 2500 rpm with a scan rate of 2 mV s^{-1}.
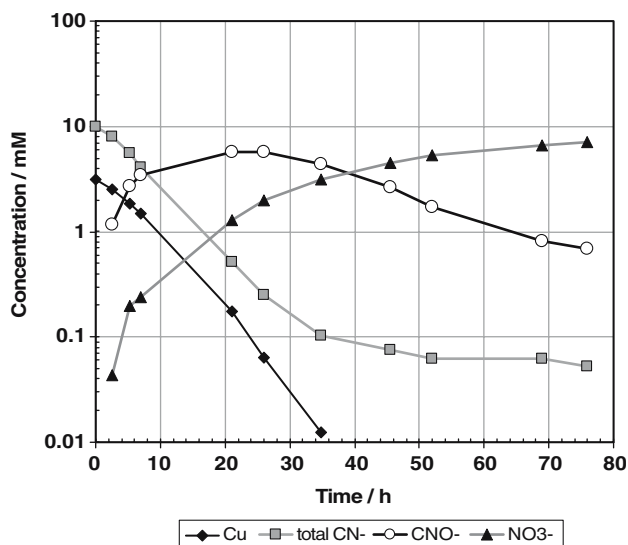

Fig. 9. Removal of copper and cyanide from synthetic solution. 2 L reservoir volume, initial current 150 mA, final current 30 mA, anode potential between 0.9 and 1.05 V vs. Hg/HgO.

CuO related cyanide oxidation followed by inhibition. While platinum and glassy carbon electrodes result in similar limiting currents (around 3 mA cm^{-2}), the current at the stainless steel electrode drops to around the same limiting current then begins to increase again starting around 0.85 V. Unfortunately in preparative electrolysis with 316 stainless steel electrodes in the same potential range, no increase in cyanide oxidation was measured, rather electrode corrosion occurred. Similar results were also obtained with the Cu$_2$S based synthetic solution. Thus, while stainless steel may be the preferred electrode material for a practical process to electrochemically treat gold ore processing wastewater due to its far lower cost, its potential would have to be carefully controlled. Otherwise, platinized titanium may be the best electrode material for such an application.

3.6. *Preparative electrolysis*

As discussed above, for a practical process, ideally stainless steel electrodes can be used with proper control of the potential between approximately 0.65 and 0.85 V (see Figure 8). However, treating wastewater containing low concentrations of copper cyanide requires large area, three-dimensional electrodes, with the additional uncertainties related to overpotential variations within the electrode structure. To investigate if this treatment approach was possible, experiments were therefore carried out using three-dimensional electrodes made from stacks of stainless steel screen. Relatively course stainless steel screen was used, both to decrease voltage variations and because a practical process needs sufficient void volume to allow for the accumulation of copper over time.

The results with synthetic alkaline copper cyanide solution are shown in Figure 9. The anode potential around 0.9 to 1.05 V was chosen to be in the best

cyanide removal region (see Figure 4). With this solution, the higher overpotential regions of the anode are coated with CuO and indeed it was noted that there was uneven deposition of copper oxide on the anodes (mostly on the 2 layers of screen closest to the cathode), indicative of problems with potential distributions. Because the CuO related catalysis acts to further increase the current coming from the higher potential regions, it will act to further accentuate uneven potential distributions in the anode structure, limiting the effective anode thickness that can be used. The copper plating at the cathode was observed to be even.

The copper and cyanide were removed to low concentrations, with the copper levels becoming undetectable after 35 h. The cyanide oxidation appears to slow after 35 h; however, concentrations below about 0.06 mM are no longer on the linear range of the ISE as we used it [35]. Even after 35 h, the anode still had a copper oxide coating and was still active, as can be seen by the further oxidation of cyanate to nitrate. Weighing the anodes and cathode after the run accounted for about 90% of the removed copper with the remainder probably lost as small pieces of the copper oxide coating which flaked off the anodes during the run. Copper appeared to be removed more effectively at the anodes (about 25% of the recovered copper was at the cathode).

Experiments with the wastewater solution gave different results (see Figure 10). After an initial delay, the copper plated evenly on the cathode. The anodes did not form a thick black copper oxide coating but instead a thin golden brown tarnish was visible on the anodes over much of the experiment. The anodes coating was more even due to the lower current flow and so less potential variation within the three-dimensional electrode. However, after about 30 h the tarnish disappeared from the electrodes. This is likely related to a slight loss in removal rate visible as a flattening of the
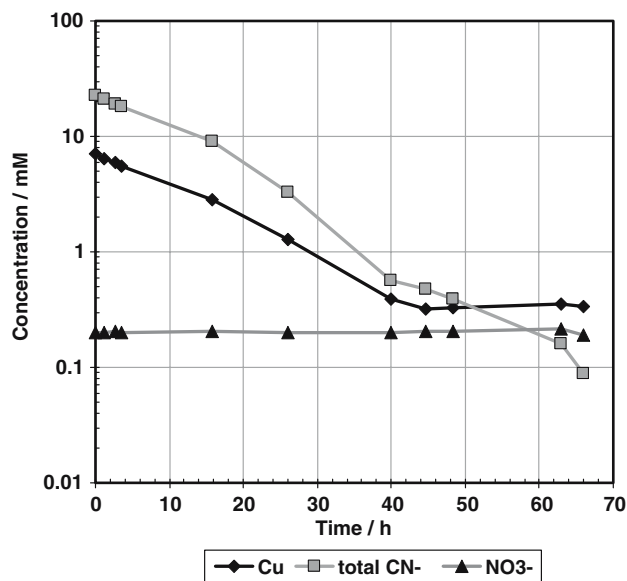
Fig. 10. Removal of copper and cyanide from wastewater sample #4. 2 L reservoir volume, initial current 60 mA, final current 2 mA, anode potential between 0.64 and 0.83 V vs. Hg/HgO.

log cyanide concentration versus time slope in Figure 10 at around 30 h. There was also a problem removing copper down to low levels, possibly due to its stabilization by other, non-cyanide, complexes. Indeed, after 50 h, the cyanide to copper ratio appears too low for copper to still be held in solutions as $[Cu(CN)_3]^{2-}$. Other causes for poor copper removal might be the lower applied voltage and the fact that, in this case, copper is only removed at the cathode. Note that due to the co-elution of cyanate and sulfite during HPLC analysis, quantification of the two compounds was not possible, although the cyanate plus sulfite peak area was observed to increase over the run. However, no nitrate formation was measured. At the end of the run, no visible corrosion of the stainless steel electrodes was observed.

The experiments thus show that with careful control of the anode potential within the 0.65 to 0.85 V window, both copper and cyanide can be removed to fairly low concentrations from sulfur containing wastewater solutions using stainless steel electrodes. This result can even be achieved using a practical, three-dimensional electrode (with its associated higher electrode voltage variation). More work, however, needs to be done to optimize the process.

4. Conclusions

The investigation of electrochemical oxidation of cyanide in wastewater from a gold ore processing operation has shown significant differences in the electrochemistry when compared to simple alkaline copper cyanide synthetic solutions. When the normal catalytic oxidation of copper cyanide to form CuO starts to occur, it is rapidly inhibited in the wastewater solutions. Instead of a typical black CuO type deposit

on the electrode, only a brown tarnish is observed. This means that, during treatment of the wastewater, the copper will be primarily removed at the cathode. The reaction inhibition appears to be related to thiocyanate and, more strongly, to copper sulfide complexes.

The limiting current found during oxidation of the wastewater is much lower than that for oxidation of simple alkaline copper cyanide. The value of the limiting current corresponds to that for free cyanide oxidation with $z_{eff} = 1$. As this reaction does not occur at a glassy carbon electrode in the potential range used in this study, some type of catalysis is therefore still occurring.

When using 316 stainless steel as an anode in solutions containing sulfur compounds, the lack of a stable CuO film leaves the stainless steel open to corrosion at higher anodic potentials. Thus, for any practical system using stainless steel electrodes, careful control of the anode potential is required.

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