Noncyanide leaching of an auriferous pyrite ore from Ecuador

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Abstract

Gold leaching of an auriferous pyrite ore from the Portovelo deposit in Ecuador indicates that noncyanide leaching systems, such as thiocyanate and thiourea, are not as effective as the traditional cyanide system. For example, whereas approximately 95% of the gold can be leached from the ore with cyanide, only about 50% gold dissolution can be achieved with a thiocyanate leaching system. Electrochemical measurements indicate that gold is not cathodically protected by pyrite in these systems. Based on the results of preliminary diagnostic experiments, it appears that gold dissolution in thiocyanate and thiourea systems is limited by passivation due to the formation of either elemental sulfur or sulfur compounds on the gold surface.

Key words: Gold leaching, Refractory ores, Thiocyanate, Thiourea

Introduction

The alkaline cyanide leaching system for gold has been studied extensively for more than 200 years, and it has been applied successfully at the industrial level for more than a century. The high recoveries, economics and simplicity of the process have made cyanide leaching of gold the preferred process, despite the necessity to pretreat certain types of ores. However, there can be some disadvantages, including high reagent consumption (Hedley and Tabachnick, 1968; Hiskey and Atluri, 1988; Sparrow and Woodcock, 1995); slow kinetics due to low oxygen solubility in water (Marsden and House, 1992; Kondos et al., 1994); and health and environmental protection issues (Kroschwitz and Howe-Grant, 1996). As a result, there has always been an interest in finding a better leaching agent for gold in terms of lower toxicity, lower reagent consumption and price, greater environmental safety, greater applicability to refractory and carbonaceous ores, and faster dissolution kinetics, among other considerations.

Alternative reagents for gold leaching include thiocyanate (SCN^-) and thiourea ($SC(NH_2)_2$). They are considered less toxic and more environmentally acceptable when compared to cyanide. One of the important features of thiocyanate and thiourea dissolution of gold is that the leaching can be performed in acidic media, enabling the use of soluble oxidizing agents, such as ferric salts.

Gold leaching requires the oxidation of the metal in the presence of a ligand that can complex gold ions and stabilize them in solution. The complexing agents are necessary because the Au^+ and Au^{+3} ions have very high standard reduction potentials, and these ions are not stable in simple aqueous solution (Hiskey and Atluri, 1988; Sparrow and Woodcock, 1995). Certain ligands, such as halides (Cl^-, Br^- and I^-), pseudohalides (SCN^- and CN^-) and carbamides ($CS(NH_2)_2$), can reduce the stability of metallic gold by the formation of stable complexes that are soluble in water. In their presence, gold can be dissolved under modest oxidizing conditions within the water stability region (Hiskey and Atluri, 1988). Gold forms aurous complexes with a coordination number of two and auric complexes with a coordination number of four. Table 1 includes the standard reduction potentials, E^0, for selected half-cell reactions. The stability constants (b) for the principal gold complexes in aqueous solutions are given in Table 2 (Hiskey and Atluri, 1988; Marsden and House, 1992).

Cyanide leaching of gold. The leaching of gold in cyanide solutions has been studied extensively by many researchers. A summary of these studies can be found elsewhere (Marsden and House, 1992; Sparrow and Woodcock, 1995). The overall reaction that describes gold dissolution in aerated, alkaline cyanide solution is
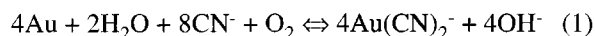
$$4Au + 2H_2O + 8CN^- + O_2 \Leftrightarrow 4Au(CN)_2^- + 4OH^- \quad (1)$$

Figure 1 shows the Eh-pH diagram for the $Au-CN-H_2O$ system at 25°C, assuming an activity of 10^{-5} for all dissolved gold species and a cyanide activity of 4×10^{-2}. These conditions are typical of subsequent experimental results discussed later in this publication. In the presence of cyanide, gold dissolves as the aurocyanide complex, $Au(CN)_2^-$. Part of its predominance area falls within the water stability boundaries, which indicates that the formation of a stable complex in aqueous solution is favorable. The Eh-pH diagram shows that thermodynamically the $Au(CN)_2^-$ complex can exist at all pH values (0 to 14). In practice, cyanide leaching is carried out at pH values of 9.5 to 11.5 (Marsden and House, 1992).

Thiocyanate leaching of gold. Thiocyanate as a leaching agent for gold has been studied by White (1905), Fleming (1986), Broadhurst and du Preez (1993), and extensively by Barbosa-Filho and Monhemius (1989, 1994a, 1994b, 1994c, 1994d). The overall reaction for gold dissolution by thiocyanate can be written as
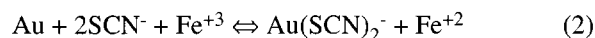
$$Au + 2SCN^- + Fe^{+3} \Leftrightarrow Au(SCN)_2^- + Fe^{+2} \quad (2)$$

Table 1 — Cathodic reactions for gold in aqueous solutions (Hiskey and Atluri, 1988; Marsden and House, 1992).

Half-cell reactions	E^0, V
Aurous half-cell reactions:	
$Au^+ + e^- = Au$	1.830
$AuCl_2^- + e^- = Au + 2Cl^-$	1.154
$AuBr_2^- + e^- = Au + 2Br^-$	0.960
$Au(SCN)_2^- + e^- = Au + 2(SCN)^-$	0.662
$AuI_2^- + e^- = Au + 2I^-$	0.572
$Au[CS(NH_2)_2]_2^+ + e^- = Au + 2CS(NH_2)_2$	0.380
$Au(CN)_2^- + e^- = Au + 2(CN)^-$	-0.606
Auric half-cell reactions:	
$Au^{+3} + 3e^- = Au$	1.520
$Au(OH)_3 + 3H^+ + 3e^- = Au + 3H_2O$	1.363
$AuCl_4^- + 3e^- = Au + 4Cl^-$	1.002
$AuBr_4^- + 3e^- = Au + 4Br^-$	0.854
$Au(SCN)_4^- + 3e^- = Au + 4(SCN)^-$	0.636
$AuI_4^- + 3e^- = Au + 4I^-$	0.560
$Au(CN)_4^- + 3e^- = Au + 4(CN)^-$	-0.440

Table 2 — Stability constants, β, for the principal gold complexes in aqueous solutions (Hiskey and Atluri, 1988; Marsden and House, 1992).

Complexes	β
Aurous complexes:	
$AuCl_2^-$	10^9
$AuBr_2^-$	10^{12}
$Au(SCN)_2^-$	1.3×10^{17}
AuI_2^-	4×10^{19}
$Au[CS(NH_2)_2]_2^+$	9.1×10^{21}
$Au(CN)_2^-$	2×10^{38}
Auric complexes:	
$AuCl_4^-$	10^{26}
$AuBr_4^-$	10^{32}
$Au(SCN)_4^-$	10^{42}
AuI_4^-	5×10^{47}
$Au(CN)_4^-$	10^{56}

Figure 1 — Eh-pH diagram for the Au-CN-H_2O system at 25°C, assuming an activity of 10^{-5} for all dissolved gold species and a cyanide activity of 4×10^{-2}.

Figure 2 — Eh-pH diagram for the Au-SCN-H_2O system at 25°C, assuming an activity of 10^{-5} for all dissolved gold species and a thiocyanate activity of 10^{-1}.

The mechanism of gold dissolution by thiocyanate in ferric sulfate solutions was found to be directly related to the oxidation of thiocyanate by the reduction of Fe^{+3} to Fe^{+2}. The oxidation of SCN^- proceeds through the formation of several intermediate species, in particular trithiocyanate $(SCN)_3^-$ and thiocyanogen $(SCN)_2$, which act as both oxidants and complexants for gold. Figure 2 presents an Eh-pH diagram for the Au-SCN-H_2O system at 25°C, assuming an activity of 10^{-5} for all dissolved gold species and a thiocyanate activity of 10^{-1} (Betts and Dainton, 1953; Barbosa-Filho and Monhemius, 1989, 1994a, 1994b, 1994c, 1994d). Thermodynamic analysis suggests that gold can be leached by thiocyanate in ferric sulfate solutions at potentials of 600 to 700 mV (SHE) at pH 1 to 3.

Thiourea leaching of gold. The use of thiourea for gold leaching has been proposed as a process alternative due to the supposed lower toxicity, faster leaching kinetics and the alleged less interference from base metals as compared to cyanide (Sparrow and Woodcock, 1995). The overall reaction that describes gold dissolution in thiourea and ferric ion solutions is
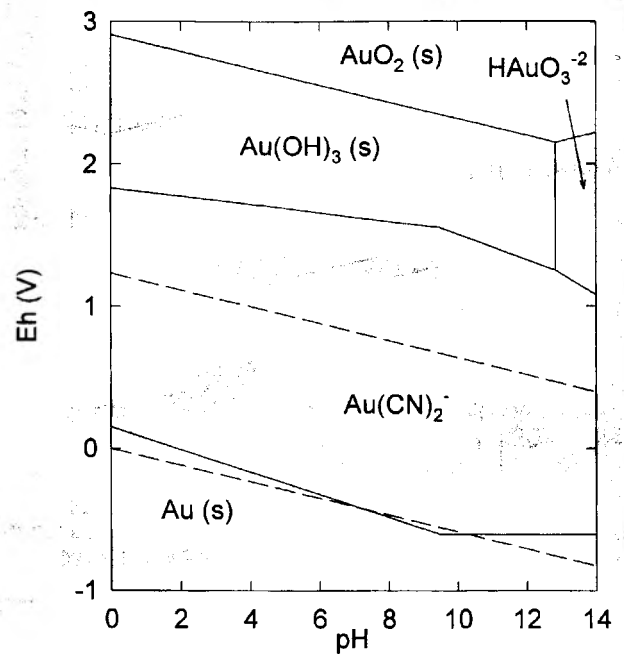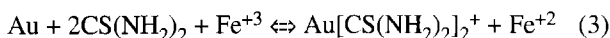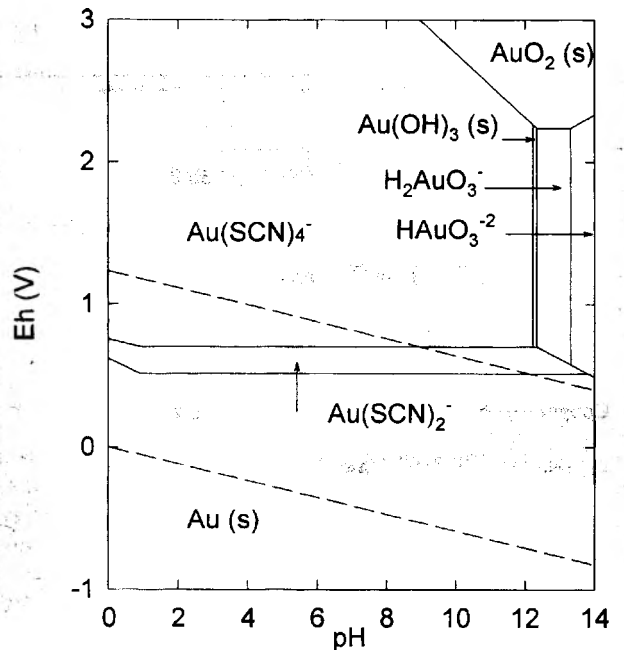
$$Au + 2CS(NH_2)_2 + Fe^{+3} \Leftrightarrow Au[CS(NH_2)_2]_2^+ + Fe^{+2} \quad (3)$$

In practice, thiourea leaching of gold is performed at thiourea concentrations of 0.13 M (10 g/L), ferric ion concentrations of 0 to 9×10^{-2} M (0 to 5 g/L), pH values of 1 to 2 and potentials between 400 and 450 mV (SHE). Higher potentials during leaching produce an oxidative degradation of thiourea into formamidine disulfide $(NH_2(NH)CSSC(NH)NH_2)$, which can decompose into thiourea $(CS(NH_2)_2)$, cyanamide (NH_2CN) and elemental sulfur (S^0). By acid hydrolysis, thiourea can decompose into urea (NH_2CONH_2) and hydrogen sulfide (H_2S). Elemental sulfur and hydrogen sulfide are undesired species during gold leaching. It is believed that both species cause a decrease in the leaching rate due to surface passivation, and H_2S may cause reprecipitation of the gold (Sparrow
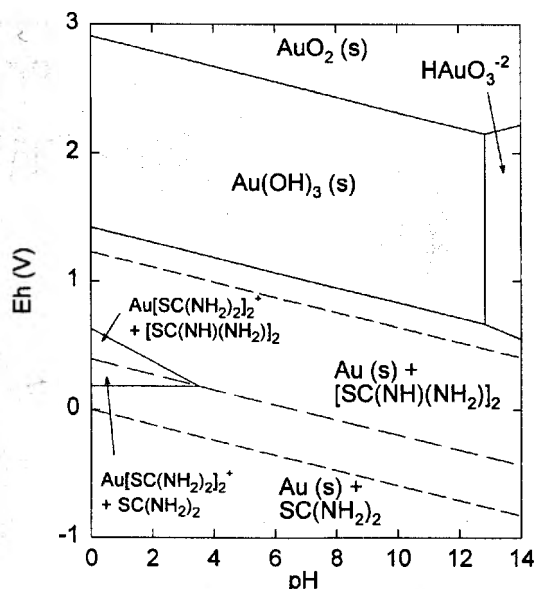
Figure 3 — Eh-pH diagram for the Au-thiourea-H_2O system at 25°C, assuming an activity of 10^{-5} for all dissolved gold species and a thiourea and formamidine disulfide activity of 1.5×10^{-1}.

Table 3 — Elemental analysis of the ore by chemical methods.

Element	Symbol	Analysis Weight %	Analysis g/t
Silicon	Si	35.9	
Sulfur	S	11.2	
Iron	Fe	8.4	
Aluminum	Al	1.7	
Zinc	Zn	0.6	
Lead	Pb	0.6	
Potassium	K	0.3	
Calcium	Ca	0.2	
Copper	Cu	0.2	
Arsenic	As		70.5
Silver	Ag		13.4
Gold	Au		7.8
Mercury	Hg		0.2

Table 4 — Mineralogical composition of the ore by XRD and polarized-light microscopy.

Mineral	Formula	Weight %
Silica	SiO_2	76.7
Pyrite	FeS_2	17.7
Sphalerite	ZnS	0.9
Galena	PbS	0.6
Chalcopyrite	$CuFeS_2$	0.5
Clays and others	–	3.6

and Woodcock, 1995). Figure 3 shows an Eh-pH diagram for the Au-thiourea-H_2O system at 25°C, assuming an activity of 10^{-5} for all dissolved gold species and a thiourea and formamidine disulfide activity of 1.5×10^{-1} (Lacoste-Bouchet et al., 1998).

Experimental procedures

Ore characteristics. The ore used in this research came from the Portovelo deposit in Ecuador. The elemental and mineralogical analyses of the ore are shown in Tables 3 and 4, respectively. Gold and silver analysis was done by fire assay, sulfur was determined by the LECO method, and the remainder of the elements was analyzed by acid digestion of a representative ore sample and atomic absorption spectrophotometry (AAS). Mineralogical analysis was done by X-ray diffraction (XRD) and polarized light microscopy in combination with a chemical balance. For a particle size distribution with a d_{80} of 74 μm, the gold distribution was 38.8% as free gold (determined by amalgamation), 56.9% as gold locked in sulfides and the remaining 4.3% as gold locked in quartz and silicates.

Leaching experiments. The leaching experiments were performed with ore that was ground and dried to yield a size distribution with a d_{80} of 74 μm. Each leaching test was started using 250 g of ore plus 750 cm³ of leaching solution (25% solids by weight) in a 1-L baffled glass vessel open to the air and at ambient temperature (23°±2°C). The pulp was agitated at 400 rpm with a stainless steel stirrer driven by an overhead motor.

In some experiments, it was desired to chemically pretreat the ore. The purpose of the pretreatment was to dissolve the metallic sulfides and liberate the gold associated with these minerals. The ground ore was oxidized with concentrated nitric acid (69.5% w/w) at 60° to 80°C in a reactor stirred at 200 rpm to keep the solids in suspension. After six hours of treatment, almost all the metallic sulfides were dissolved with only the silicates and gold remaining. This oxidized ore was washed thoroughly to eliminate any residual acid and then dried. Because of the chemical pretreatment, the ore weight decreased by about 22.5%. The chemical pretreatment of 250 g of ore produced approximately 190 g of oxidized material that was added to 750 cm³ of leaching solution (20% solids by weight).

Sample analysis. At certain times, a 25- to 30-cm³ pulp sample was taken to analyze metal dissolution and reagent consumption. The sample was taken using a 2-mm-ID-diam that had one of its ends permanently submerged in the slurry and the other attached to a 50-cm³ syringe. After the residual hold-up volume was purged with air, a volume of 30 cm³ of slurry was loaded into the syringe and discharged again to the system through the hose before the sample was taken for analysis. The sample was filtered using Whatman No. 1 filter paper. Generally, the determination of gold dissolution and reagent consumption was performed by analysis of the aqueous phase. In some cases, additional analysis of the remaining solids was required. For this purpose, the solids from the sample were washed with deionized water after filtration and were dried at 60°C for four hours. Gold in the solid samples was analyzed, after acid digestion, by solvent extraction with Aliquat 336 in di-isobuthyl ketone (DIBK) (Groenewald, 1968).

With this solvent-extraction method, gold analysis by AAS is very accurate and eliminates the possible interference of other metals; however, it was not applicable to gold-thiocyanate solutions. Several tests performed with solutions of a known concentration of gold containing thiocyanate showed low gold extraction to the organic phase. Therefore, it was necessary to perform the gold analysis with calibration standards that were prepared with concentrations of thiocyanate and total iron similar to the samples to be analyzed and at pH 2, to avoid matrix interference. Free cyanide was analyzed using the Liebig-Déniges method (Dorr, 1936). Free thiocy-

anate was analyzed using the Volhard method (Ashword, 1975). Total iron was determined by AAS. Ferrous iron was determined by titration with potassium permanganate in the presence of sulfuric acid (Vogel, 1960). To avoid interference of other oxidizable species that may consume permanganate, such as thiocyanate, ferrous ion was determined using the same aliquot after thiocyanate precipitation with silver nitrate, which was added in excess to assure complete precipitation of the thiocyanate ion. Gold in thiourea solution was determined by AAS. Free thiourea was determined by titration with potassium iodate (Yatsimirrsky and Ashateva, 1958).

Polarization tests. Polarization tests were performed using an electrochemical cell and a three electrode system in the range of -1.0 to 1.0 V (SHE). A platinum electrode was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode. The working electrodes were a gold electrode, with a surface area of 0.28 cm^2, and a pyrite electrode, with a surface area of 1.21 cm^2. For each working electrode, the values of current density for the corresponding potential were obtained with an EG&G Applied Research Potentiostat-Galvanostat, Model 273. A freshly prepared leaching solution previously purged with argon for one hour was used in each polarization test.

Experimental results and discussion

Cyanide leaching. Figure 4 shows the results for gold leaching at initial sodium cyanide concentrations, i.e., $[NaCN]_0$, of 0.02 M (0.98 g/L) and 0.04 M (1.96 g/L), 23°C and pH 11. In the first six hours of leaching, 89.6% of the gold present in the ore was dissolved in a solution with $[NaCN]_0$ of 0.02 M. In the remaining 18 hours of leaching, an additional 4.1% was dissolved, resulting in 93.7% gold dissolution in 24 hours, with a total sodium cyanide consumption of 0.36 kg/t ore. An increase of $|NaCN]_0$ to 0.04 M did not significantly increase the overall gold dissolution. During the first six hours, 91.0% of the gold present in the ore is dissolved, and, during the remaining 18 hours of leaching, an additional 6.6% is dissolved, resulting in 97.6% gold dissolution in 24 hours, with a total sodium cyanide consumption of 1.50 kg/t ore. As expected, the leaching rate is rather insensitive to the cyanide concentration. Under these conditions, the leaching rate depends on soluble oxygen availability (Thompson et al., 1999).

Thiocyanate leaching. The variables for this study were the concentration of the lixiviant, added as sodium thiocyanate (NaSCN), the concentration of the oxidant, added as ferric sulfate nonahydrate ($Fe_2(SO_4)_3 \cdot 9H_2O$), and ore chemical pretreatment, as shown in Table 5. All experiments were carried out at pH 2.

Thiocyanate leaching without chemical pretreatment of the ore: Figure 5 illustrates the effect of $[Fe^{+3}]_0$ and $[SCN^-]_0$ on the overall gold dissolution from the ore without chemical pretreatment. The results show that, for the range of variables studied, gold dissolution was dependent on both $[SCN^-]_0$ and $[Fe^{+3}]_0$. For both the low (0.04 M) and the high (0.08 M) values of $[Fe^{+3}]_0$, higher gold dissolution was achieved at the high value of $[SCN^-]_0$ (0.10 M). An overall higher gold dissolution was achieved with the higher $[Fe^{+3}]_0$ for both of the initial thiocyanate concentrations. In all cases, the reagents were significantly in excess of that required for gold dissolution, and, thus, the extent of reaction is not limited by reactant depletion, as will be demonstrated later.

Chemical analysis of the solutions taken during the leaching experiments showed that there was an increase of total iron
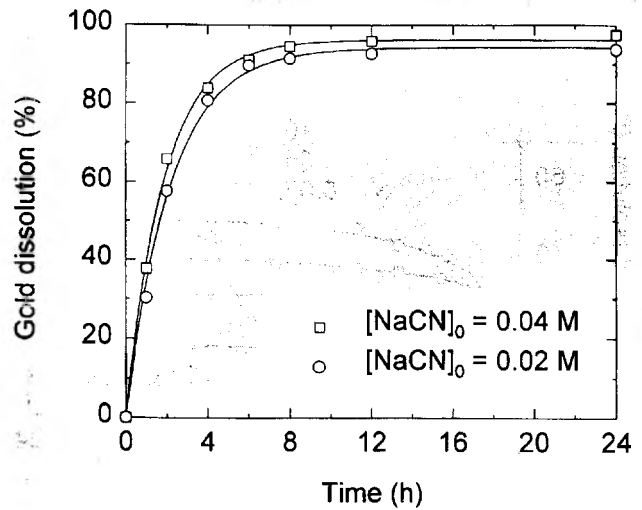

Figure 4 — Gold dissolution vs. time at different initial sodium cyanide concentrations, 23°C, pH 11, 400 rpm, and 25% solids by weight.

Table 5 — Results after 24 hours of thiocyanate leaching at 23°C, pH 2, 400 rpm, 25% solids by weight for the ore without chemical pretreatment and 20% solids by weight for the ore with pretreatment.

Test	$[SCN^-]_0$ M	$[Fe^{+3}]_0$ M	Dissolved Au%	$\Delta[Fe]^*$ %	NaSCN cons., kg/t
Without	0.05	0.04	18.3	10.0	0.6
pretreatment	0.05	0.08	31.2	10.1	1.1
	0.10	0.04	40.5	13.0	0.6
	0.10	0.08	49.5	12.3	1.1
With	0.05	0.04	63.5	–	0.26
pretreatment	0.05	0.08	66.3	–	0.26
	0.10	0.04	84.6	–	0.52
	0.10	0.08	84.3	–	0.39

*Increase of total iron in solution

in solution ($\Delta[Fe]$) of about 10% to 13% after 24 hours of leaching. This means that the acidic thiocyanate-ferric sulfate system not only leached gold from the ore but also dissolved iron from the pyrite. This is not surprising, as it is known that in acidic media, ferric iron leaches sulfides to produce elemental sulfur under certain circumstances (Dutrizac and MacDonald, 1974; Free, 1992) according to

$$MS + 2Fe^{+3} = 2Fe^{+2} + M^{+2} + S^0 \qquad (4)$$
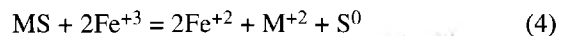
Thiocyanate leaching with chemical pretreatment of the ore: Figure 6 illustrates the effect of $[Fe^{+3}]_0$ and $[SCN^-]_0$ on the overall gold dissolution from the ore with chemical pretreatment. It shows that, for the range of variables studied, gold dissolution was dependent on $[SCN^-]_0$ and less dependent on $[Fe^{+3}]_0$. For both the low (0.04 M) and the higher (0.08 M) values of $[Fe^{+3}]_0$, higher gold dissolution was achieved at the high value of $|SCN^-]_0$ (0.10 M). The initial ferric ion concentration was found to have little effect on the gold dissolution. For all the combinations of $[SCN^-]_0$ and $[Fe^{+3}]_0$ studied, the percentage of overall gold dissolution obtained from the ore with pretreatment was higher than for the ore without chemical pretreatment. For the ore with chemical pretreatment, a maximum of 84.6% of the gold present in the
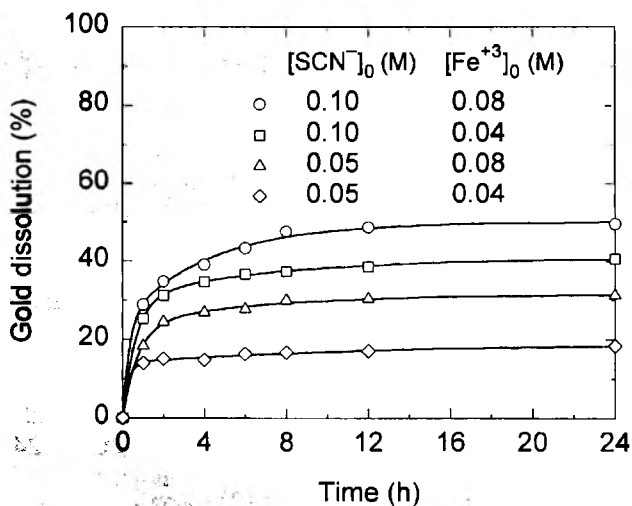
Figure 5 — Gold dissolution vs. time for the ore without chemical pretreatment at different concentrations of thiocyanate and ferric ion at 23°C, pH 2, 400 rpm, and 25% solids by weight.
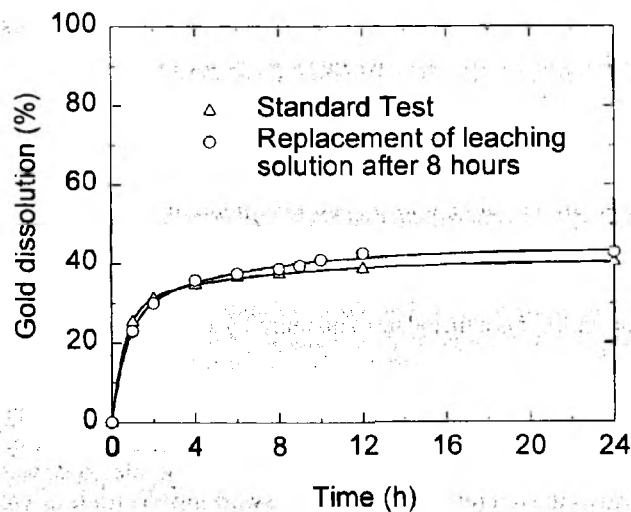

Figure 7 — Gold dissolution vs. time for the ore without chemical pretreatment with 0.10 M [SCN⁻], and 0.04 M [Fe⁺³]₀, 23°C, pH 2, 400 rpm, and 25% solids by weight.
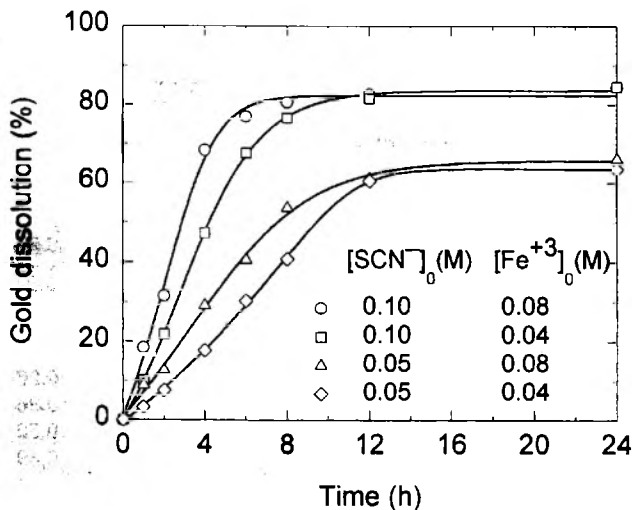

Figure 6 — Gold dissolution vs. time for the ore with chemical pretreatment at different concentrations of thiocyanate and ferric ion at 23°C, pH 2, 400 rpm, and 20% solids by weight.

ore can be leached in 24 hours, compared to a maximum of 49.5% for the ore without pretreatment. The dissolution rate was faster during the first two hours of leaching for the ore without pretreatment than it was for the ore with chemical pretreatment. During the next hour, the dissolution rate decreased for the ore without chemical pretreatment until it reached an equilibrium at four hours of leaching for $[SCN^-]_0$ of 0.05 M and at eight hours of leaching for $[SCN^-]_0$ of 0.10 M. In the case of the ore with chemical pretreatment, the gold dissolution rate tended to be linear during the first 12 hours for $[SCN^-]_0$ of 0.05 M and during the first four hours for $[SCN^-]_0$ of 0.10 M.

Additional thiocyanate experiments. Three additional experiments involving the thiocyanate system were performed to investigate the possibility of galvanic protection of gold by pyrite. These were the composition of the lixiviant during leaching, the presence of free gold and electrochemical measurements.

Composition of the lixiviant: To determine the effect of the composition of the lixiviant on gold dissolution, the ore was leached for eight hours with 0.10 M $[SCN^-]_0$ and 0.04 M $[Fe^{+3}]_0$. The pulp was then filtered, and the ore was washed and dried. Leaching was then revived with fresh lixiviant having the same initial composition as that used initially for an additional 16 hours. After the change to fresh lixiviant, only an additional 2.4% of the total gold contained in the ore was dissolved, as shown in Fig. 7.

Presence of free gold: To determine the effect of the presence of free gold on gold dissolution, the ore was leached with 0.10 M $[SCN^-]_0$ and 0.04 M $[Fe^{+3}]_0$. After eight hours of leaching, 3 mg of free metallic gold with an average particle diameter of 100 μm were added to the leaching slurry. The test was continued for 16 additional hours, and about 85% of the free gold added to the system was dissolved by the residual leaching solution after 24 hours of leaching.

Electrochemical measurements: The possibility that gold and pyrite were forming a galvanic cell, where pyrite was being dissolved in preference to gold, was considered through electrochemical measurements. A galvanic cell is formed when a metal is electrically coupled with another metal (or conducting nonmetal) in the same electrolyte. During galvanic coupling, dissolution of the metal with a lower reduction potential occurs as its surface becomes anodic, while dissolution of the metal with a higher reduction potential ceases as its surface becomes cathodic. An Evans diagram that shows gold and pyrite oxidation and Fe^{+3} reduction in 0.1M $[SCN^-]_0$ and 0.08 M $[Fe^{+3}]_0$ at pH 2 is presented in Fig. 8. The potential at which pyrite dissolution occurs by ferric reduction is above the potential at which gold dissolution occurs by ferric reduction. This means that, from a thermodynamic standpoint, gold dissolution should occur in preference to pyrite dissolution. In other words, the results suggest that gold will not be cathodically protected by pyrite.

Recall that the total weight percent of dissolved gold with 0.1 M $[SCN^-]_0$ and 0.08 M $[Fe^{+3}]_0$ from the ore without chemical pretreatment is similar to the amount of free gold present in the ore (49.5% and 38.8%, respectively). When the pyrite and other sulfides were dissolved from the ore, gold dissolution increased up to 84.3%. The results obtained from the first two experiments suggest that the thiocyanate-ferric sulfate system was able to dissolve free gold. Also, it is evident that the leaching solution is able to dissolve gold when free metallic gold is added to the system, and that the gold
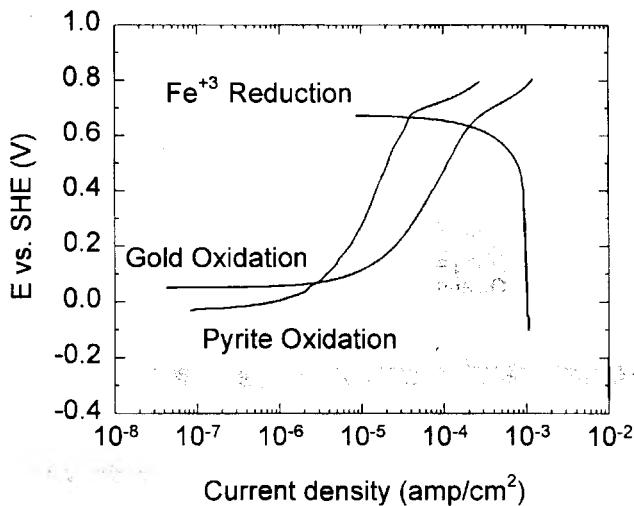
Figure 8 — Evans diagram showing the anodic oxidation of gold and pyrite electrodes and the cathodic reduction of Fe^{+3} at a gold electrode surface in 0.1M $[SCN^-]_0$ and 0.08 M $[Fe^{+3}]_0$ at pH 2.

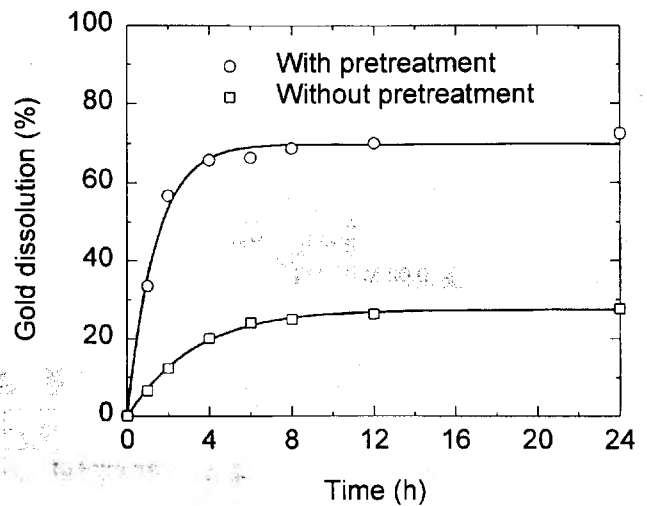**Figure 9** — Gold dissolution vs. time with 0.15 M $[SC(NH_2)_2]_0$ and 0.02 M $[Fe^{+3}]_0$, 23°C, pH 2, 400 rpm, and 20% solids for the ore with chemical pretreatment, and 25% solids for the ore without chemical pretreatment.

locked in pyrite was protected somehow from dissolution; although it is not likely that this was due to galvanic protection, based on the electrochemical experiments.

Thiourea leaching. To compare gold dissolution from the ore with and without pretreatment for another lixiviant, the system of thiourea-ferric sulfate was chosen. Figure 9 shows the results for gold leaching at $[SC(NH_2)_2]_0$ of 0.15 M (11.4 g/L) and $[Fe^{+3}]_0$ of 0.02 M (1.12 g/L) and pH 2. As with the thiocyanate lixiviant, gold dissolution of the ore without chemical pretreatment was very low, compared to the ore with pretreatment. Without chemical pretreatment, 27.6% of the gold was dissolved, while with chemical pretreatment, the overall dissolution was 72.5%. Thiourea consumption was high in both cases: 38.3 and 36.8 kg/ton for the ore without and with chemical pretreatment, respectively.

Comparison of cyanide, thiocyanate and thiourea systems. Figure 10 compares the results obtained by all three systems after 24 hours of leaching of the ore without pretreatment. Cyanide leaching with 0.04 M $[CN^-]_0$ at pH 11 resulted in a better overall gold dissolution (97.6%) than thiocyanate leaching with 0.10 M $[SCN^-]_0$ and 0.08 M $[Fe^{+3}]_0$ at pH 2 (49.5% gold dissolution) or thiourea leaching with 0.15 M $[SC(NH_2)_2]_0$ and 0.02 M $[Fe^{+3}]_0$ at pH 2 (27.6% gold dissolution).

Presence of sulfur-reaction product. The presence of a sulfur-reaction product in the thiocyanate-ferric sulfate system and in the thiourea-ferric sulfate system was investigated by scanning electron microscopy and energy dispersed spectroscopy (SEM-EDS). Square gold foils, 2 by 2 mm square and 0.025 mm thick, were placed in 300 cm³ of leaching solution of the composition given in Table 6. After eight hours of treatment, the foils were washed carefully with deionized water and dried under a nitrogen atmosphere. The foils were analyzed for sulfur by SEM-EDS, and the results are shown in Table 6. The depth of penetration of the 20 kV beam used for these analyses was estimated in less than 0.71 μm.

To determine if elemental sulfur was formed after 8 hours of leaching the ore with the thiocyanate and thiourea systems at pH 2, 10 g of solid residues were treated with 20 cm³ of carbon disulfide (CS_2) after acid washing and thermal pretreatment of the residues at 100°C for one hour. Carbon
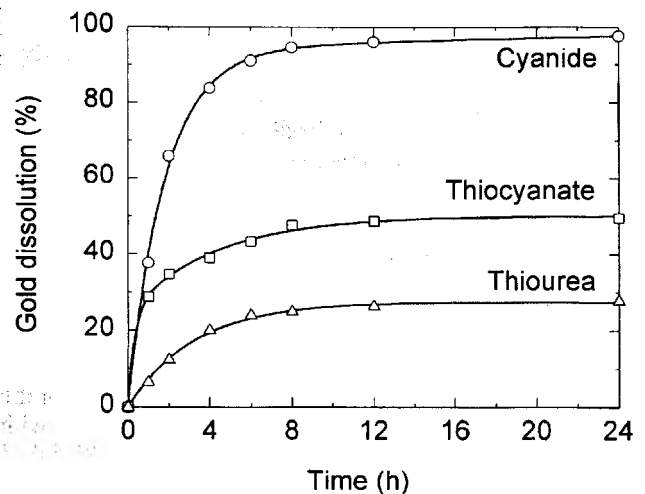

Figure 10 — Comparison of the leaching results for the ore without chemical pretreatment with different lixiviants at 23°C, 400 rpm and 25% solids by weight: Cyanide leaching with 0.04 M $[CN^-]_0$ at pH 11; Thiocyanate leaching with 0.10 M $[SCN^-]_0$ and 0.08 M $[Fe^{+3}]_0$ at pH 2; Thiourea leaching with 0.15 M $[SC(NH_2)_2]_0$ and 0.02 M $[Fe^{+3}]_0$ at pH 2.

disulfide dissolves elemental sulfur, and it can be recovered by evaporation of the CS_2. The results showed in Table 7 indicate that elemental sulfur was formed during the leaching of the ore. Elemental sulfur was not found in the original ore before leaching. A test performed with 10 g of ore where 0.2 g of elemental sulfur was added, showed 96.7% of sulfur recovery with this method.

The results suggest that, during gold leaching of the pyrite ore with thiocyanate-ferric sulfate and thiourea-ferric sulfate at pH 2, elemental sulfur is formed. This sulfur appears to cause passivation of the gold, probably due to the formation of a thin sulfur layer on the gold surface, which significantly limits gold dissolution in these leaching systems.

Conclusions

Thiocyanate-ferric sulfate and thiourea-ferric sulfate leaching of gold from an auriferous pyrite ore of the Portovelo deposit in Ecuador, with 38.8% of the gold present as free gold, was evaluated. Experimental results showed that, at pH

Table 6 — SEM-EDS analysis for gold foils after 8 hrs of leaching in different solutions with and without ore.

Leaching solution	Ore presence	Presence of sulfur
0.1 M[SCN⁻]₀, 0.08 M [Fe⁺³]₀	Yes	Less abundant
0.1 M [SCN⁻]₀, 0.08 M [Fe⁺³]₀	No	Least abundant
0.15 M [SC(NH₂)₂]₀, 0.02 M [Fe⁺³]₀	Yes	Most abundant
0.15 M [SC(NH₂)₂]₀, 0.02 M [Fe⁺³]₀	No	More abundant
0.02 M [CN⁻]₀	Yes	No
0.02 M [CN⁻]₀	No	No

Table 7 — Elemental sulfur formation during leaching.

Leaching solution at pH 2	Amount of sulfur recovered, Weight %
$0.05\ M\ [SCN^-]_0,\ 0.04\ M\ [Fe^{+3}]_0$	0.142
$0.05\ M\ [SCN^-]_0,\ 0.08\ M\ [Fe^{+3}]_0$	0.187
$0.10\ M\ [SCN^-]_0,\ 0.04\ M\ [Fe^{+3}]_0$	0.098
$0.10\ M\ [SCN^-]_0,\ 0.08\ M\ [Fe^{+3}]_0$	0.150
$0.15\ M[SC(NH_2)_2]_0,\ 0.02\ M\ [Fe^{+3}]_0$	0.205

2, with initial concentrations of sodium thiocyanate of 0.10 M (8.1 g/L) and ferric ion of 0.08 M (4.5 g/L), 49.5% of the gold present in the ore was dissolved after 24 hours of leaching without chemical pretreatment in a stirred-tank reactor. The dissolution of gold was faster during the first hours of leaching and then decreased to a slower rate. After chemical pretreatment of the ore to dissolve the sulfides present, gold dissolution increased to 84.3% using the same initial leaching conditions. In the case of the $0.15\ M\ [SC(NH_2)_2]_0$ and $0.02\ M\ [Fe^{+3}]_0$ system at pH 2, gold dissolution did not exceed 27.6% for the ore without pretreatment and reached 72.5% for the ore with pretreatment. In contrast to these results, 93.7% and 97.6% of the gold present in the Portovelo ore was leached, without oxidative pretreatment, by sodium cyanide solutions with initial concentrations of 0.02 M (1 g/L) and 0.04 M (2 g/L) at pH 11. These findings indicate that the thiocyanate-ferric sulfate and thiourea-ferric sulfate systems for gold leaching from this auriferous pyritic ore are not as effective as the traditional cyanide system. From several diagnostic experiments, it has been shown that the thiocyanate-ferric sulfate and thiourea-ferric sulfate leaching solutions produce elemental sulfur or sulfur compounds, and it is hypothesized that these species form a protective layer on the gold surface, inhibiting its dissolution.

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